Russian Chemical Reviews **71** (11) 917 – 927 (2002) © 2002 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2002v071n11ABEH000745

Norbornadiene – quadricyclane as an abiotic system for the storage of solar energy

A D Dubonosov, V A Bren, V A Chernoivanov

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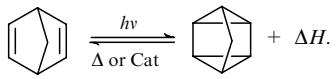
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Abstract. Data on the valence isomerisation of norbornadiene and its derivatives into the corresponding quadricyclanes published between 1990 and 2001 are considered and described systematically. The applicability of this reaction for the storage of solar energy is discussed. The bibliography includes 112 references.

I. Introduction

About ten years have passed since the publication of our review [1] in which the norbornadiene – quadricyclane system was considered as a promising accumulator and converter for solar energy. However, the interest in the problem of solar energy accumulation has not slackened. This results from the fact that irreplaceable natural energy sources, *i.e.*, coal, oil and natural gas, are still being consumed almost without control;[2–4] furthermore, the problems related to climate changes on the Earth due to the emission of enormous amounts of carbon dioxide, as well as products of incomplete combustion of natural fuel, into the atmosphere are becoming ever more critical.[5]

The possible ways to utilise solar energy are extremely diverse.[6,7] They include the use of solar energy to perform various photocatalytic processes,[8–10] photodecomposition of water and photolytic production of hydrogen,[11,12] as well as various photobiological processes, including artificial photosynthesis.[13–15] An alternative abiotic approach to the transformation of solar energy is to accumulate it as the strain energy in metastable photoinduced isomers of organic compounds. The norbornadiene – quadricyclane system is most promising for this purpose.[16,17] Its advantage is that the valence isomerisation of bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, NBD) (**1**) into tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (quadricyclane, Q) (**2**) better fits the requirements for organic photochromes intended as solar energy accumulators.[1]



1 **2**

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Received 24 June 2002
Uspekhi Khimii **71** (11) 1040 – 1050 (2002); translated by S S Veselyi

The photoisomerisation of NBD results in a metastable quadricyclane structure containing highly strained cyclobutane and two cyclopropane fragments. As a result, the reverse thermal or catalytic reaction **2** → **1** is characterised by a considerable thermal effect ($\Delta H = -89$ kJ mol^{-1}) (see Ref. 18), which is greater than the ΔH value for other photochromic systems. There is a wide range of homo- and heterogeneous catalysts that enable this reaction to be performed and hence thermal energy to be evolved,[1,16] but the high activation barrier to the thermal transformation **2** → **1** (even at 140 °C, the half-life period of quadricyclane **2** is 14 h)[19] makes it possible to store the accumulated solar energy for a long time.

However, the system **1** → **2** has a number of considerable drawbacks. First, the longwave absorption edge of non-substituted NBD **1** (λ_{ae}, $\varepsilon = 1$ litre mol^{-1} cm^{-1}) is no higher than 300 nm.[20] Second, the quantum yield (Φ) of the valence isomerisation **1** → **2** in the absence of sensitising agents is ~ 0.05 (see Refs 20, 21). In order that this system could be used on industrial scale as a solar energy accumulator, one has to chemically modify NBD for shifting the values of λ_{ae} towards the maximum of the light energy of the Sun (400 – 600 nm) and at the same time for increasing the photoisomerisation quantum yield. This review presents a generalisation of the studies that dealt with this problem and were carried out between 1990 and 2001. The following general directions can be distinguished: (1) the use of sensitisers for the valence isomerisation **1** → **2**, including those chemically bound to the NBD molecule; (2) modification of the structure of the starting NBD to increase λ_{ae} and Φ; (3) the use of various polymeric systems containing NBD (or its derivatives) in the lateral or main chain of the macromolecule, as well as polymer-bound sensitisers.

II. Photosensitisation of the valence isomerisation of norbornadiene into quadricyclane

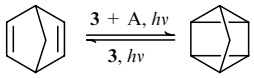
As a rule, the isomerisation **1** → **2** involves the triplet state of NBD.[22–25] Therefore, at the initial stage of the studies under discussion, the photosensitisation was performed mostly by various carbonyl compounds (acetophenone, propiophenone, benzophenone, acridinone, Michler's ketone and some others) known as triplet sensitisers (S).[24–27] Since the energy of the triplet state (E_T) of NBD is very high (~ 257 kJ mol^{-1}),[22,28] only a small number of sensitisers with high E_T fit the classical triplet – triplet transfer scheme:

$$S \xrightarrow{h\nu} {}^1S \longrightarrow {}^3S \xrightarrow{NBD} S + {}^3NBD \longrightarrow S + {}^3Q \longrightarrow S + Q.$$

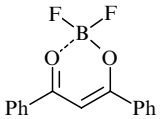
Irradiation is normally carried out in the absorption band of the sensitiser, which is first converted to a singlet excited state ^{1}S and then, through intersystem crossing, to the triplet state ^{3}S. The triplet–triplet energy transfer to NBD is followed by its adiabatic isomerisation into ^{3}Q and then relaxation to the ground state (Q). The highest quantum yields $\Phi_{\mathbf{1}\rightarrow\mathbf{2}}$ were obtained using acetophenone (0.91, λ_{ae} = 366 nm, E_T = 301 kJ mol^{-1}) and benzophenone (0.45, λ_{ae} = 380 nm, E_T = 290 kJ mol^{-1}); in the latter case, photoacoustic calorimetry revealed the formation of ^{3}NBD with a life-time of $\sim$ 7 ns.[25] However, the use of sensitisers of this type for solar energy storage by means of the photoreaction **1** → **2** was quite limited in recent years. This is due to both difficulties associated with the selection of new systems with E_T values not exceeding 257 kJ mol^{-1} and the formation of side addition products of sensitisers to norbornadiene or quadricyclane.[29–33] Therefore, the main attention of researchers was paid to the use of metal complexes[6] or derivatives of carbonyl compounds[31] with E_T < 257 kJ mol^{-1}. In this case, the sensitisation of the photoreaction **1** → **2** occurs through a stage which involves the formation of sensitiser–norbornadiene complexes in electron-excited states:[23, 25, 34]

$$S \xrightarrow{h\nu} {}^1S \longrightarrow {}^3S \xrightarrow{NBD} [{}^3S\cdots NBD] \longrightarrow S + Q.$$

Most commonly, the products are exciplexes or charge-transfer complexes; however, more complicated structures can be formed, *e.g.*, triplexes.[31] Cooperative (combined) sensitisation is carried out using the fluoroborate complex **3** (BFC) in combination with aromatic hydrocarbons (A), namely, toluene, ethylbenzene, biphenyl or durene.[35]



1 **2**



3

The use of the sensitiser **3** alone is not efficient, as the reaction of the singlet-excited ^{1}BFC with norbornadiene or quadricyclane results in radical cations NBD$^{+\bullet}$ and Q$^{+\bullet}$. The latter is readily rearranged to NBD$^{+\bullet}$, as its energy level is 38–46 kJ mol^{-1} lower than the level of Q$^{+\bullet}$ (see Refs 36, 37). If a co-sensitiser A is added, the process changes basically: the radical ion pair is stabilised and a triplet-excited state is realised; the latter then decomposes to ^{3}NBD, which undergoes recombination into quadricyclane.

$$BFC \xrightarrow{h\nu} {}^1BFC \longrightarrow$$

$$\longrightarrow {}^1[BFC\cdots BFC] \longrightarrow 2\,BFC$$

$$\xrightarrow{NBD} {}^1[BFC\cdots NBD] \longrightarrow {}^1[BFC^{-\bullet}\cdots NBD^{+\bullet}] \longrightarrow BFC + NBD$$

$$\xrightarrow{A} {}^1[BFC\cdots A] \xrightarrow{NBD} {}^1[BFC^{-\bullet}\cdots(A\cdots NBD)^{+\bullet}] \rightleftharpoons$$

$$\rightleftharpoons {}^3[BFC^{-\bullet}\cdots(A\cdots NBD)^{+\bullet}] \longrightarrow BFC + A + {}^3NBD \longrightarrow Q$$

Efficient sensitisation of the **1** → **2** transformation due to electron transfer without formation of triplet-excited ^{3}NBD is observed in the presence of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTA):[25]

$$BTA \xrightarrow{h\nu} {}^1BTA \longrightarrow {}^3BTA \xrightarrow{NBD} [BTA^{-\bullet}\cdots NBD^{+\bullet}] \longrightarrow$$

$$\longrightarrow BTA + {}^3Q \longrightarrow Q.$$

The quantum yield of the reaction (in $CDCl_3$) is $\sim$ 0.9. *N*-(α-Naphthyl)carbazole (NCA) increases the efficiency of the **1** → **2** isomerisation owing to intramolecular charge transfer from the carbazole moiety of the sensitiser molecule in the excited state to the naphthyl radical. In this case, these fragments turn so as to become mutually perpendicular [the so-called Twisted Intramolecular Charge Transfer (TICT) state].[38]

$$NCA \xrightarrow{h\nu} {}^1[NCA] \longrightarrow {}^1[N^{-\bullet}-CA^{+\bullet}] \longrightarrow {}^3[NCA] \longrightarrow$$

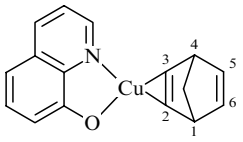
TICT

$$\longrightarrow {}^3[NCA\cdots NBD] \longrightarrow NCA + Q.$$

Metal complex sensitisers of the Rh(phen)$_3^{3+}$ type (phen is 1,10-phenanthroline),[34] which can form exciplexes with NBD, shift the λ_{ae} values to the $\leqslant$ 400 nm region, but the quantum yield of the photoreaction is low ($\Phi \approx 0.01$). Metal complexes which can form complexes with NBD in the ground state are more efficient:

$$S + NBD \longrightarrow [S\cdots NBD] \xrightarrow{h\nu} S + Q.$$

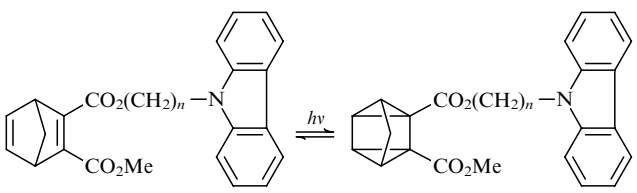
Such complexes are characterised by an intense charge transfer band in the region λ > 300 nm where the starting sensitiser and NBD do not have considerable absorption.[39–41] Excitation of NBD complexes with $[CuCl(PR^1_2R^2)]_n$ (R^1 , R^2 = Et, 2-MeC$_6$H$_4$, 4-MeC$_6$H$_4$, C$_6$F$_5$CH$_2$) in THF with light with a wavelength (λ_{irr}) of 366 nm gives quadricyclanes with quantum yields Φ = 0.03–0.49. The use of $[Cu_2L_2(\mu\text{-NBD})]$ complexes [where L is 2-methyl-8-quinolinolato, 5,7-dichloro-2-methyl-8-quinolinolato, 4-acridinolato, 2-(benzotriazol-2-yl)-4,5-di-*tert*-butylphenolato] allows irradiation to be carried out in a longer-wave spectral region (λ_{irr} = 405 nm).[39] Although the quantum yield of the formation of quadricyclane is rather low (Φ = 0.029), the number of Q molecules formed per S molecule is $\sim$ 5000. This fact makes the above system very promising for the practical storage of solar energy. Although sensitisation of the **1** → **2** photoreaction with univalent copper compounds is well known,[1] the mechanism of this process could not be explained theoretically until recently.[42] An *ab initio* method (B3LYP) was used to study the geometry of the ground state of the complex **4**, *i.e.*, NBD bound to CuL as the sensitiser (L is 8-quinolinolato).



4

The calculated geometrical parameters of the system **4** agree well with the values obtained by X-ray diffraction analysis.[39] It is of note that the C(2)=C(3) bond in the complex **4** is elongated to 1.409 Å in comparison with the similar bond in non-substituted NBD (1.339 Å). Analysis of the electronic structure of the adduct **4** makes it possible to conclude that the interaction of NBD with the sensitiser is in fact donation of the π-electrons of the copper atom to the π*-antibonding orbital of NBD, which decreases the π–π*-splitting in the norbornadiene fragment from 5.91 to 3.36 eV. Owing to this, complexes of the type **4** can absorb light in the visible spectral region, which makes them applicable for the storage of the sunlight.

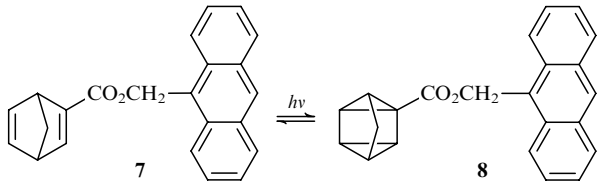
The covalent binding of norbornadiene to a sensitiser makes it possible to avoid side addition photoreactions of the sensitiser to NBD or polymerisation of NBD. Photoinduced intramolecular electron transfer from the carbazole moiety of molecule **5** to carbon–carbon double bonds of the norbornadiene fragment ($\lambda_{irr} \geqslant$ 350 nm) favours the efficient formation of quadricyclane **6**.[43]



5 **6**

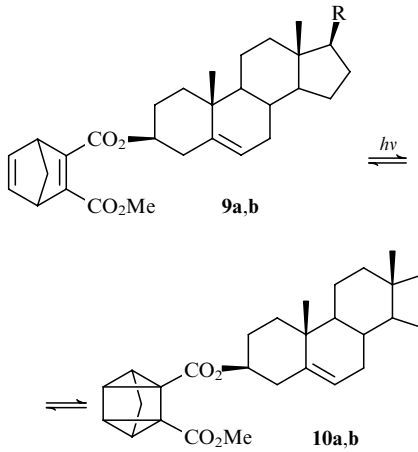
n = 2, 6.

The intramolecular energy transfer from the second triplet (*via* the T_2 state) of the anthracene fragment to the norbornadiene moiety of compound **7** causes its isomerisation to quadricyclane **8**.[44] This mechanism was proven using two-photon flash-photolysis (λ^1_{exc} = 260 – 290 nm, λ^2_{exc} > 410 nm); the quantum yield of the photoreaction in benzene is 0.022.



7 **8**

In the past decade, intense studies were carried out on the photophysical and photochemical features of intramolecular processes of energy or electron transfer through a rigid steroid bridge (SB), which links benzophenone (BP) or benzidine (BZ) with a norbornadiene molecule.[45–48] For example, the dichromophoric 3β-{[2-(methoxycarbonyl)bicyclo-[2.2.1]hepha-2,5-dien-3-yl]carbonyloxy}androst-5-en-17β-ylbenzophenone-4-carboxylate (**9a**, NBD – SB – BP) undergoes isomerisation upon steady-state irradiation (λ_{irr} > 350 nm) to give a photo-product **10a** (Q – SB – BP) with a quantum yield Φ = 0.038.

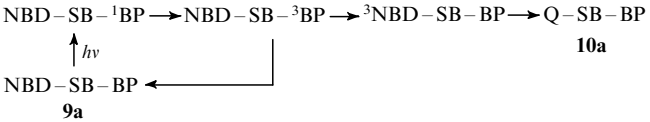


9a,**b**

10a,**b**

a: R = OCO–⟨⟩–CO–⟨⟩; **b**: R = Me(Me)N–⟨Me,Me⟩–⟨Me,Me⟩–NMe$_2$.

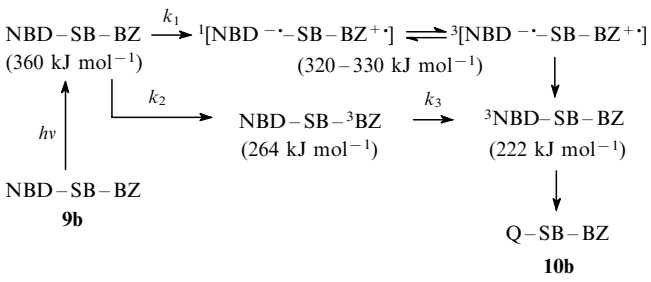
It should be noted that only the benzophenone chromophore can absorb irradiation under these conditions. Singlet-excited benzophenone forms the triplet state ^{3}BP by fast and efficient intersystem crossing. The main pathway of ^{3}BP deactivation involves triplet – triplet energy transfer to the norbornadiene fragment through the system of σ-bonds of the steroid bridge.



10a

9a

The quantum yield of isomerisation of 3β-{[2-methoxycarbonyl)bicyclo[2.2.1]hepta-2,5-dien-3-yl]carbonyloxy}androst-5-en-17β-yl-2,2′,6,6′,*N*,*N*′,*N*′-heptamethylbenzidine (**9b**, NBD – SB – BZ) in cyclohexane is 0.07 (λ_{irr} > 300 nm), with quantitative formation of the photo-product **10b** and with no side reactions. In this case, the isomerisation scheme suggested by Tung *et al.*[45] involves not only the triplet – triplet energy transfer but also the formation of a triplet radical-ion state, which then undergoes recombination to the triplet-excited state of NBD.



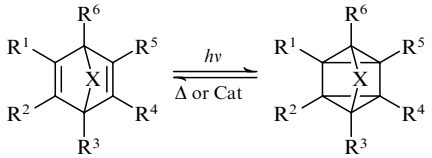
9b **10b**

The rate constants for the corresponding steps are as follows: $k_1 = 1.1 \times 10^7$ s^{-1}, $k_2 = 5.2 \times 10^7$ s^{-1}, $k_3 = 5.2 \times 10^5$ s^{-1} (the values in parentheses correspond to the energies of the states with respect to the ground state of compound **9b**).

The latter examples of valence isomerisation open a new approach to sensitisation, in which a coloured chromophore sensitiser that is remote from the norbornadiene fragment can undergo photoexcitation.

III. 'Donor – acceptor' norbornadienes

Non-substituted NBD is a formally non-conjugated, non-planar, strained diene. The steric strain in its molecule allows through-space interaction of the C=C bond π-orbitals.[49–51] As a result, non-substituted NBD absorbs light in a longer-wave spectrum region than two isolated C=C bonds. The systems **11** in which the interaction of electron-donating substituents at one of the carbon – carbon double bonds in the molecule with electron-withdrawing substituents at another bond results in a low-intensity charge transfer band ($\varepsilon < 10^2$ litre mol^{-1} · cm^{-1}) were called 'donor – acceptor' NBD.[52] The long-wave absorption edge of these compounds (λ_{ae}) can be as high as 500 – 560 nm.

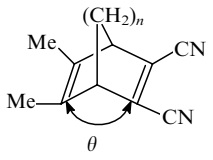


11 **12**

X = CH_2, CMe_2; R^1, R^2 = H, Me, Ph, 4-$MeOC_6H_4$;

R^4, R^5 = CN, CO_2Me, CO_2Et, CONHPh; R^3, R^6 = H, Me.

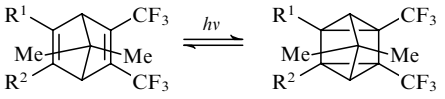
The geometrical structure and electronic absorption spectrum of norbornadiene were studied [53–55] with consideration of indirect conjugation of double bonds and π,σ-interaction. This interaction was observed experimentally when studying the electronic absorption spectra of bicyclo[2.2.*n*]alka-2,5-dienes **13**.[52]



13

When *n* changes from 3 to 1, the angle θ decreases gradually. This is accompanied by a bathochromic shift of the long-wave absorption band (λ_{max}) from 305 to 338 nm with simultaneous increase in the molar extinction coefficient (ε_{max}) from 178 to 200 litre mol^{-1} cm^{-1}. The value of λ_{ae} in the spectra of norbornadienes **11** can be as high as 560 nm, while the quantum yields of the photoreaction **11** → **12** are high (Φ = 0.26 – 0.75). However, despite high Φ values, the applicability of compounds **11** for the storage of solar energy is limited due to the following factors: (1) the low extinction coeficient ($\varepsilon_{max} \approx 1000$ litre mol^{-1} s^{-1}) makes the efficiency of the **11** → **12** process low and requires prolonged exposure to light; (2) many quadricyclanes **12** are unstable at room temperature and undergo spontaneous rear-

rangement to the original NBD **11**. Although some attempts to increase the thermal stabilities of quadricyclanes by introduction of perfluoroalkyl substituents have been undertaken a long time ago,[56] it is only in recent years that reliable methods for the synthesis of the 'donor–acceptor' NBD **14** have been developed; the latter are not only thermally stable at room temperature but also absorb solar energy quite efficiently (Table 1).[57, 58]



14 **15**

R^1, R^2 = 4-$MeOC_6H_4$, 4-$Me_2NC_6H_4$, 2-benzofuryl, 2-thienyl.

Table 1. Spectral characteristics of norbornadienes **14** and thermal stabilities of quadricyclanes **15**.[57, 58]

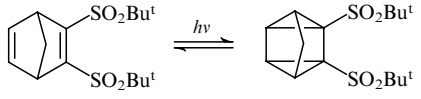
Compound **14**	R^1	R^2	λ_{max} /nm ($10^{-4}\,\varepsilon_{max}$ /litre mol^{-1} cm^{-1})	λ_{ae} /nm	$\tau_{1/2}$ [a] /h
a	4-$MeOC_6H_4$	4-$MeOC_6H_4$	346 (0.51)	440	see [b]
b	4-$Me_2NC_6H_4$	4-$Me_2NC_6H_4$	390 (0.85)	510	9600
c	4-$Me_2NC_6H_4$	4-$MeOC_6H_4$	374 (0.85)	500	see [b]
d	4-$Me_2NC_6H_4$	2-thienyl	385 (0.78)	520	500
e	2-benzofuryl	2-benzofuryl	414 (2.00)	480	72
f	4-$Me_2NC_6H_4$	2-benzofuryl	407 (1.29)	580	31

[a] Half-life of quadricyclane. [b] Quadricyclane is stable at 20 °C.

Unlike compounds **11**, norbornadienes **14** have high values of ε_{max} ranging from 5000 to 20 000 litre mol^{-1} cm^{-1}. Their absorption edge increases as the electron-donating properties of the substituents R^1 and R^2 increase; in fact, λ_{ae} = 580 nm for norbornadiene **14a**. The thermal stabilities of quadricyclanes **15** are sufficiently high for the practical storage of solar energy; the number of cycles **14** ⇋ **15** reaches 10^3 without considerable destruction of the starting compound.

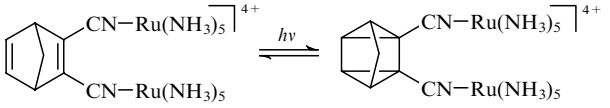
IV. 2,3-Disubstituted norbornadienes

The synthesis of 'donor–acceptor' norbornadienes faces considerable difficulties: polysubstituted cyclopentadiene derivatives and disubstituted acetylene derivatives are first synthesised and then brought into the Diels–Alder reaction. 2,3-Disubstituted norbornadienes can also be synthesised from non-substituted cyclopentadiene and 1,2-disubstituted acetylene. The studies carried out over the past ten years have shown that in many cases, the presence of an electron-donating substituent and an electron-withdrawing substituent at one of the two double bonds of the norbornadiene molecule is sufficient for their spectral and photochemical characteristics not to be inferior, and sometimes even to be superior, to the corresponding parameters of the 'donor–acceptor' NBD. Two substituents of the same nature shift the λ_{ae} value only slightly towards the solar radiation maximum.[59, 60] For example, the absorption of 2,3-di(*tert*-butylsulfonyl)norbornadiene (**16**) is characterised by a slight bathochromic shift with respect to the maximum absorption of non-substituted NBD **1**, although the **16** → **17** isomerisation occurs quantitatively in ether under irradiation with light with λ_{irr} > 280 nm.



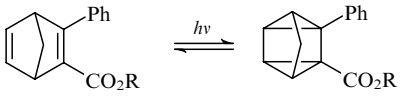
16 **17**

The valence isomerisation of the 2,3-dicyanonorbornadiene–pentaamminoruthenium(II) complex **18** is an exception.[61] The long-wave absorption maximum of norbornadiene **18** in methanol is observed around 490 nm ($\varepsilon \approx 14\,000$ litre mol^{-1} s^{-1}); the λ_{ae} is 700 nm, but the quantum yield of the formation of the quadricyclane **19** upon irradiation with light with λ_{irr} = 500 nm is as low as 8.3×10^{-4}.



18 **19**

Combination of an electron-withdrawing and an electron-donating substituents at one of the carbon–carbon double bonds in NBD favours an increase in the isomerisation quantum yield. The electronic absorption spectra and the quantum yields of the phototransformation of 3-phenylnorbornadiene-2-carboxylic acid (**20a**) and its esters **20b–d** are listed in Table 2.[62, 63] Although these systems absorb in the spectral region λ < 360 nm, the fast and quantitative photoisomerisation **20** → **21**, which takes a few seconds in DMSO, acetonitrile, ethanol and THF ($c = 5 \times 10^{-5}$ mol $litre^{-1}$), allows us to consider the norbornadienes **20** to be an efficient system for the accumulation of solar energy.



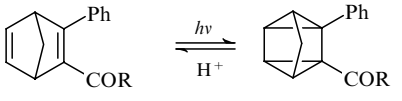
20a–d **21a–d**

R = H (**a**), CH_2Ph (**b**), $CH_2C_6H_4OMe$-4 (**c**), $(CH_2)_6OC_6H_4OMe$-4 (**d**).

Table 2. Spectral characteristics of norbornadienes **20** and quantum yields of the photoreactions **20** → **21** in acetonitrile.[62, 63]

Compound **20**	R	λ_{max} /nm ($10^{-4}\,\varepsilon_{max}$ /litre mol^{-1} cm^{-1})	λ_{ae} /nm	Φ (λ_{irr} = 284 nm)
a	H	291 (1.12), 222 (0.66)	–	0.32
b	$PhCH_2$	292 (0.56)	350	0.36
c	4-$MeOC_6H_4CH_2$	297 (0.74), 225 (2.45)	355	0.27
d	4-$MeOC_6H_4O(CH_2)_6$	291 (0.71), 224 (1.62)	340	0.25

2-Trifluoroacetyl-3-phenylnorbornadiene (**22**) absorbs light at $\lambda_{ae} \leqslant 460$ nm; its photoisomerisation into the quadricyclane **23** in benzene occurs quantitatively with a quantum yield $\Phi = 0.62–0.86$ (depending on the starting concentration of norbornadiene).[64, 65]



22, **24** **23**, **25**

R = CF_3 (**22**, **23**), NHAr (**24**, **25**).

Involvement of the carbon–carbon double bond of norbornadiene in the conjugation chain Ph–C=C–CONHR affects the λ_{ae} and Φ values even more significantly.

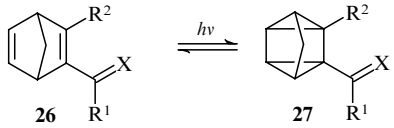
We have studied the spectral and photochemical features of 3-phenylnorbornadiene-2-carboxamides **24**.[66, 67] Compounds **24** are characterised by absorption in the region 280–305 nm (Table 3) and λ_{ae} = 375–435 nm.[66, 67] Irradiation with light with a wavelength corresponding to the long-wave absorption maximum (λ_{irr} = 313 nm) results in their isomerisation to give quadricyclanes **25** with high quantum yields. Electron-withdrawing substituents in the *N*-phenyl ring increase the Φ value in comparison with non-substituted 3-phenyl-2-(*N*-phenylcarbamoyl)norbornadiene **24a**, whereas electron-donor substituents decrease this

Table 3. Spectral characteristics of 3-phenylnorbornadiene-2-carboxamides **24** and quadricyclanes **25** and quantum yields of the photoreaction **24** → **25** in propan-2-ol.[66, 67]

Compound **24**	R	λ_{max} /nm ($10^{-4}\varepsilon_{max}$ /litre mol^{-1} cm^{-1})	λ_{ae}(**24**) /nm	Φ (λ_{irr} = 313 nm)	λ_{ae}(**25**) /nm
a	Ph	233 (1.98), 280 (0.9)	375	0.53	295
b	4-MeC_6H_4	232 (1.78), 285 (0.78)	380	0.46	295
c	2-MeC_6H_4	229 (1.74), 280 (0.76)	380	0.49	295
d	4-MeOC_6H_4	235 (1.33), 290 (0.76)	400	0.15	310
e	4-MeCOC_6H_4	221 (1.30), 295 (1.28)	380	–	370
f	4-EtO_2CC_6H_4	278 (0.93), 310 (0.74)	380	0.71	310
g	3-$NO_2C_6H_4$	232 (2.28), 305 (0.87)	390	0.66	300
h	α-naphthyl	223 (1.47), 295 (0.28)	380	0.0	–
i	β-naphthyl	234 (3.78), 300 (1.00)	380	0.22	320

value. However, it should be noted that as electron-withdrawing groups are introduced, the λ_{ae} values of norbornadienes **24** become closer to those of quadricyclanes **25**, hence the efficiency of solar energy accumulation decreases. The quadricyclanes obtained upon valence isomerisation **24** → **25** are stable at room temperature and in the presence of acid catalysts. In the presence of MoO_3 as a heterogeneous catalyst, they undergo rearrangement to the original NBD with a rate constant of $k = 5\times10^{-2}-10^{-3}$ s^{-1} at 293 K.

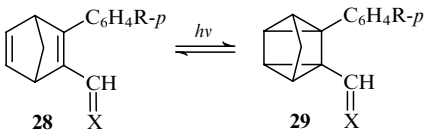
Since the triplet mechanism of isomerisation of norbornadiene into quadricyclane can occur with high quantum yields in the presence of aromatic ketones, we studied norbornadienes **26** with one of the C=C bonds involved in the conjugation chain of the Ph–C=C–C=X fragment (Table 4).[67–71]



R^1 = H, Me, OMe, CH=CHPh; R^2 = Br, Ar; X = O, CHCOAr.

Irradiation of NBD **26** in propan-2-ol at a wavelength corresponding to the maximum absorption in the long-wave region (λ_{irr} = 313 or 365 nm) results in quadricyclane structures **27**. Absorption at the highest wavelengths is observed in the case of 2-[2-(3-nitrobenzoyl)vinyl]-3-phenylnorbornadiene (**26l**): its absorption edge approaches 500 nm while the quantum yield of isomerisation is rather high (Φ = 0.25). The highest value Φ = 0.60 is observed for norbornadiene **26f**. Quadricyclanes **27** are stable at 293 K; however, they readily undergo isomerisation into the original compounds under conditions of homogeneous catalysis if a small amount of trifluoroacetic acid ($10^{-2}-10^{-3}$ mol litre^{-1}) is added to their solutions in heptane (5×10^{-5} mol litre^{-1}). Since heterogeneous catalysis is more suitable for practical solar energy accumulation,[1] it seemed reasonable to study the effect of oxides, *viz*., V_2O_5, WO_3 and MoO_3, on quadricyclanes **27**. The best catalytic activity was observed for molybdenum(VI) oxide, which is characterised by the highest metal electronegativity in this series.[72] Stirring of solutions of quadricyclanes **27** in heptane (5×10^{-5} mol litre^{-1}) with MoO_3 (0.2–0.5 mg per 2 ml of a solution) results in the original norbornadienes **26** with a rate constant $k = 10^{-2}-5\times10^{-3}$ s^{-1} at 291 K. Conditions for the repeated phototransformation **26** ⇋ **27** have been determined. The calculated turnover number with the loss of the working substance not exceeding 3% is $8\times10^2-10^3$.

Elongation of a conjugation chain involving one of the double bonds in norbornadiene may be a way to increase the λ_{ae} and Φ values. In view of this, we studied the spectral and photochemical properties of 3-arylnorbornadiene-2-carbaldehyde derivatives **28**, namely, oximes, imines, hydrazones, *etc*. (Table 5).[67, 69, 71, 72] By varying the electron-donating and electron-withdrawing substituents at the C=C double bond in norbornadienes **28**, it became possible to shift the values of λ_{max} to 500 nm and λ_{ae} to 620 nm. Heterogeneous catalysis with Mo(VI) oxide described above proved to be efficient for the reverse reaction of the majority of quadricyclanes **29**.



R = H, NO_2, NH_2; X = NOH, NOMe, NAr, NNPh, $C(CN)_2$, $C(CN)CO_2Et$, $C(CO_2Et)_2$.

Table 4. Spectral characteristics of carbonyl-containing norbornadienes **26** and quadricyclanes **27** and quantum yields of the photoreaction **26** → **27** in propan-2-ol.[67–71]

Compound **26**	X	R^1	R^2	λ_{max} /nm ($10^{-4}\varepsilon_{max}$ /litre mol^{-1} cm^{-1})	λ_{ae}(**26**) /nm	Φ [a]	λ_{ae}(**27**) /nm
a	O	H	Ph	222 (1.44), 318 (0.96)	400	0.40	330
b	O	Me	Ph	250 (0.89), 297 (0.92)	400	0.34	350
c	O	Ph	Br	259 (1.02), 286 (0.39)	360	0.33	330
d	O	CH=CHPh	Ph	300 (2.48), 345 (1.10)	435	–	420
e	CHCOPh	H	Ph	231 (1.70), 377 (1.69)	450	0.10	415
f	CHCOPh	H	4-$NO_2C_6H_4$	263 (2.03), 387 (2.26)	470	0.60	400
g	O	OMe	4-$NO_2C_6H_4$	322 (1.53)	415	0.01	380
h	O	OMe	4-$NH_2C_6H_4$	237 (1.70), 353 (2.07)	445	0.20	330
i	$CHCOC_6H_4$Me-4	H	Ph	375 (1.63)	470	0.12	410
j	$CHCOC_6H_4$Cl-4	H	Ph	258 (4.09), 380 (1.72)	475	0.15	420
k	$CHCOC_6H_4$Br-4	H	Ph	257 (3.76), 381 (1.68)	475	0.16	420
l	$CHCOC_6H_4NO_2$-3	H	Ph	250 (3.15), 389 (1.55)	500	0.25	420
m	$CHCOC_6H_4$Ph-4	H	Ph	275 (3.12), 390 (1.89)	500	0.08	440

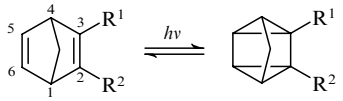
[a] For compounds **26a**–**c**,**g**, λ_{irr} = 313 nm; for compounds **26d**,**h**, 365 nm; for compounds **26e**,**f**,**i**–**m**, 436 nm.

Table 5. Spectral characteristics of norbornadienes **28** and quadricyclanes **29** and quantum yields of the photoreaction **28** → **29** in propan-2-ol.[67, 69, 71, 72]

Compound **28**	R	X	λ_{max} /nm ($10^{-4}\,\varepsilon_{max}$ /litre mol^{-1} cm^{-1})	λ_{ae}(**28**) /nm	Φ [a] (λ_{irr} = 436 nm)	λ_{ae}(**29**) /nm
a	H	NOH	223 (1.68), 310 (1.36)	360	0.19	310
b	H	NOMe	227 (1.70), 313 (1.48)	370	0.16	330
c	H	NPh	235 (2.16), 343 (1.66)	425	0.15	350
d	H	NC_6H_4OMe-4	238 (2.86), 365 (2.37)	465	0.12	360
e	H	$NC_6H_4NMe_2$-4	252 (1.70), 320 (1.51), 405 (2.00)	525	0.10	400
f	H	NNHPh	257 (1.67), 373 (3.06)	455	0.05	370
g	H	$C(CN)_2$	251 (1.39), 303 (0.60), 382 (2.15)	480	0.74	330
h	NO_2	$C(CN)_2$	302 (1.79), 386 (2.98)	480	0.75	340
i	NH_2	$C(CN)_2$	235 (1.58), 282 (2.44), 505 (3.62)	620	0.10	380
j	H	$C(CN)CO_2Et$	249 (1.62), 298 (0.62), 376 (2.18)	490	0.69	360
k	H	$C(CO_2Et)_2$	233 (1.75), 350 (0.76)	430	0.63	330

[a] For compounds **28a**–**c**,**k** , λ_{irr} = 365 nm.

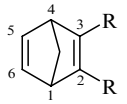
More complete data on the effect of substituents on the state of C=C double bonds in norbornadiene were obtained from an X-ray diffraction study of compounds **28c** and **28g** (see Ref. 73) and comparison with literature data on the structure of non-substituted NBD [53, 74] and 2-(2,2-diphenylvinyl)norbornadiene-3-carboxylic acid **30**.[75]



1, **28c**,**g**, **30** **2**, **29c**,**g**, **31**

Compounds	R^1	R^2
1, **2**	H	H
28c, **29c**	Ph	CH=NPh
28g, **29g**	Ph	$CH=C(CN)_2$
30, **31**	CO_2H	$CH=CPh_2$

The lengths of single bonds in the molecule **28c** have ordinary values (1.57 Å on average), but the lengths of the C(2)=C(3) (1.342 Å) and C(5)=C(6) double bonds (1.310 Å) differ markedly from the lengths of similar bonds in non-substituted NBD **1** (1.333 Å). X-Ray diffraction data suggest that the C(2)=C(3) bond is conjugated with the azomethine C=N bond and with the π-bonds in the phenyl substituents; this results in its elongation with simultaneous shortening of the C(5)=C(6) bond. In the molecule **28g**, which contains a stronger electron-withdrawing substituent, the C(2)=C(3) bond is elongated considerably [to 1.38(1) Å], whereas the C(5)=C(6) bond is shortened [to 1.29(2) Å]. The quantum yield of this photoreaction increases in the order: 0.05 (**1**) < 0.15 (**28c**) < 0.74 (**28g**). A similar pattern of changes in the lengths of double bonds was found for norbornadiene **30**;[75] the C(2)=C(3) bond in this molecule is elongated to 1.359 Å due to the conjugation with the π-systems of the substituents, while the C(5)=C(6) bond is shortened to 1.271(4) Å. The presence of two electron-withdrawing substituents at the C=C double bond in norbornadienes **32a**,**b** affects the distribution of the bond lengths less significantly.[76, 77] For example, the elongation of the C(2)=C(3) bond in the molecule of 2,3-dicyanonorbornadiene (**32a**) is insignificant [to 1.339(2) Å], whereas the C(5)=C(6) bond is shortened to 1.315 Å [in the molecule **32b**, the lengths of these bonds are 1.341(3) and 1.285(4) Å, respectively].

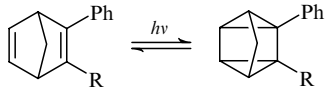


32a,**b**

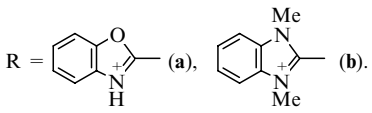
R = CN (**a**), $CONH_2$ (**b**).

X-Ray diffraction data suggest convincingly that if one of the double bonds in norbornadiene is involved in a conjugation chain with an electron-donating and an electron-withdrawing substituents, its length increases in parallel with the λ_{ae} and Φ values.

In view of this, it seemed attractive to use organic cations as the electron-withdrawing component, although it has been shown previously [78, 79] that the presence of pyridinium or pyrylium cations gives high values of λ_{ae} and Φ but results in irreversible opening of the cyclopropane fragment in the quadricyclanes formed. We have studied the photochemical properties of 2-benzooxazolyl and 2-benzoimidazolyl derivatives of 3-phenylnorbornadiene **33a**,**b**.[67, 69, 80] The benzooxazole derivative **33a** is characterised by λ_{ae} = 550 nm, but the **33a** → **34a** rearrangement occurs irreversibly. The λ_{ae} value for the benzoimidazolyl derivative **33b** is 340–365 nm, depending on the type of the counter ion (I^-, ClO_4^-, BF_4^-, $SbCl_6^-$), while the quantum yield of the photoreaction is 0.41–0.45. None of the known catalysts of the reverse reaction [1] affects quadricyclanes **34b**, whereas thermal initiation (343 K, solution in acetonitrile) results in the original NBD with a rate constant $k = 6 \times 10^{-4}$ s^{-1}, with complete restoration of the original spectrum. The cycle **33b** ⇋ **34b** can be repeated many times.

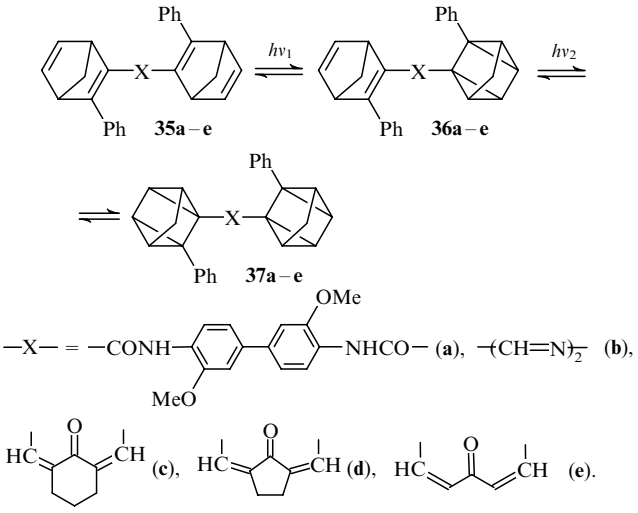


33a,**b** **34a**,**b**



In order to increase the amount of accumulated solar energy per mol of the original compound, we have studied the dinorbornadiene systems **35a**–**e**.[81] Dinorbornadienes **35a**–**e** absorb light in the region of 345–450 nm; the λ_{ae} values for compounds **35c**–**e** are as high as 530–560 nm. Irradiation of these compounds with light with a wavelength of 365 nm (**a**, **b**) or 436 nm (**c**–**e**) results in valence isomerisation into the corresponding monoquadricyclanes **36** and then into diquadricyclanes **37**. The two-step pattern of the photoreaction postulated previously for dinorbornadienyl derivatives of diamides [82] was confirmed for 3-phenylnorbornadiene-2-carbaldazine (**35b**). The primary photoproduct **36b** is characterised by a new absorption band at 380 nm (λ_{irr} = 436 nm, Φ = 0.023); its subsequent irradiation with a wavelength within this band (λ_{irr} = 365 nm, Φ = 0.028) gives the diquadricyclane **37b**. The reverse transformation into the original dinorbornadienes can be carried out under conditions of homogeneous or

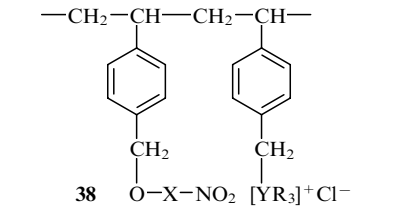
heterogeneous catalysis (addition of CF_3CO_2H or MoO_3, respectively).



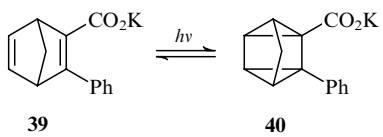
V. Polymer-bound norbornadienes and sensitisers

One of the leading approaches to the accumulation of solar energy developed in recent years involves the use of polymeric systems containing non-substituted NBD or its derivatives in a lateral or main chain of the macromolecule as well as polymer-bound sensitisers of the valence isomerisation NBD → Q. This is primarily due to the fact that norbornadiene fragments incorporated in a polymer are more stable than free NBD molecules with the same substituents. In many cases, this makes it possible to avoid side reactions and to increase the quantum yield of NBD → Q photoisomerisation and the turnover number.

The first studies along this direction were aimed at the synthesis of polymer-bound benzophenone or acetophenone, but the photo-stability of such sensitisers proved to be rather low.[83,84] Polymeric photosensitisers of a new type (**38**) containing ammonium or phosphonium groups (for binding the substrate) together with sensitising nitroaryloxy groups were used to carry out the **39** → **40** photoisomerisation.[85]

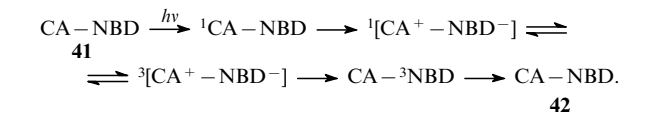


—X— = , ; Y = P, N; R = Pr^n, Bu^n, n-C_6H_{13}.

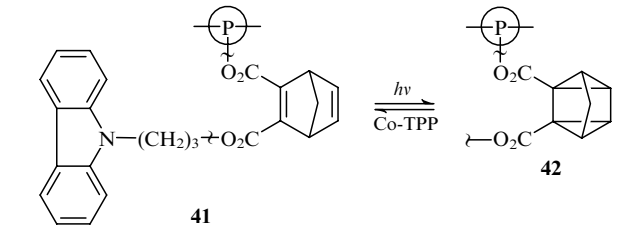


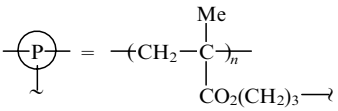
The quantum yield of this reaction was 0.19 at λ_{irr} = 366 nm in the absence of a sensitiser and 0.42 in the presence of the polymer **38**, suggesting that intermolecular energy transfer occurred from the sensitiser (**38**) to the norbornadiene (**39**).

Irradiation of the polymers **41** in the visible spectral region (λ_{irr} > 350 nm) results in their valence isomerisation into the quadricyclane derivatives **42**.[86] A mechanism of this process was suggested, which involved the intramolecular electron transfer from the carbazole (CA) sensitiser to the norbornadiene fragment:

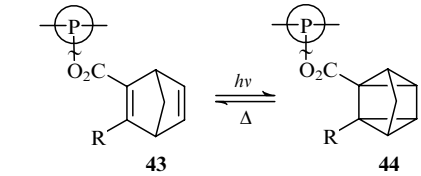


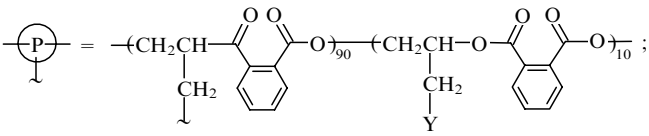
The reverse reaction occurs in the presence of catalytic amounts of (5,10,15,20-tetraphenyl-21*H*,23*H*-porphyrinato)-cobalt(II) (Co-TPP).





The valence isomerisation of polyesters **43** containing benzophenone and norbornadiene fragments occurs both in polymeric films and in solutions in dichloromethane (Φ = 0.62 – 0.84) and involves a stage of efficient energy transfer from the sensitiser to NBD.[87] Compounds **44** are rather stable; the reverse reaction **44** → **43** releases ~90 kJ mol^{-1} of the accumulated thermal energy.

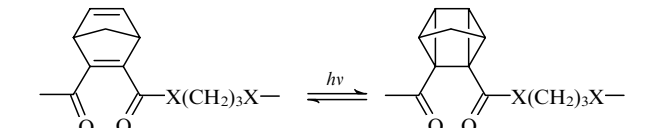




Y = O—CO—, N(Me)—CO— ,

N(Me)—CO—NMe2; R = CON , $CONPr^n_2$, CO_2Me.

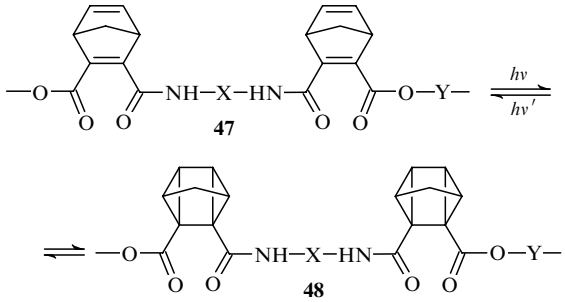
Polyamides **45** containing non-substituted norbornadiene fragments in the main chain are characterised by values $\lambda_{ae} \leqslant 440$ nm.[88–90] Irradiation of these compounds in this spectral region results in the selective isomerisation of NBD into quadricyclanes without side reactions. Incorporation of a sensitiser, *e.g.*, Michler's ketone or 4-(*N*,*N*-dimethylamino)benzophenone, in the polymer increases the efficiency of the **45** → **46** process. The reverse transformation occurs upon addition of Co-TPP to a solution of the polyamide **46** in dichloromethane or upon irradiation of polymeric films of **46** with light with λ_{irr} = 235 – 260 nm.



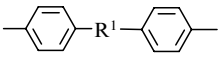
—X— = —N , —N N— , —HNH2C CH2NH— ,

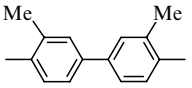
—NH(CH2)6NH— , —N H— Y —N H— ; Y = CH_2, O.

Polyesters **47** with similar composition also readily undergo photoisomerisation on exposure to sunlight in polymeric films or as solutions in THF to give quadricyclane derivatives **48**.[91]

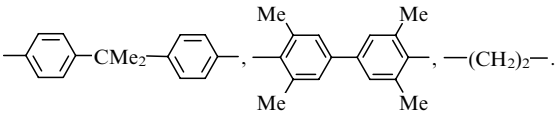


47 ⇌ **48**

—X— = ;

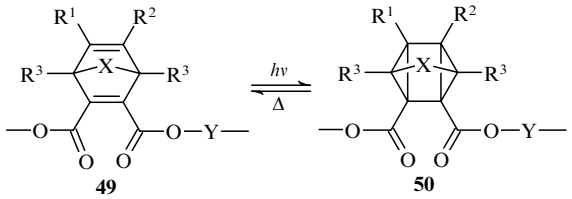
—R¹— = —CH₂—, —O—, ;

—Y— = —CH₂CH(OH)CH₂OR²OCH₂CH(OH)CH₂—;

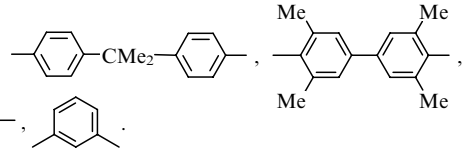
—R²— = .

The reverse transformation of solid polymers **48** occurs efficiently under irradiation with light with $\lambda_{irr} = 272$ nm and is accompanied by liberation of heat (~84 kJ mol^{-1}).

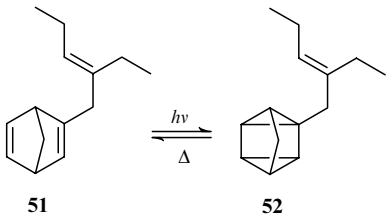
'Donor–acceptor' NBD can also be incorporated in the main chain of a polymeric molecule.[92,93] Owing to the existence of a charge transfer band, polyesters **49** have $\lambda_{ae} \leqslant 500$ nm. Irradiation of polymeric films of compound **49** with visible light yields isomeric compounds **50**; the reverse reaction occurs slowly at room temperature.



49 ⇌ **50**

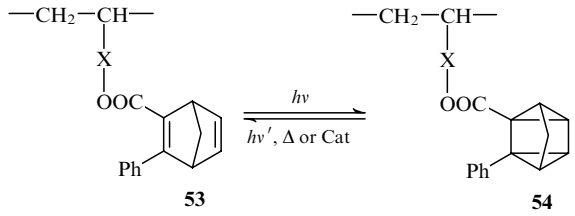
—X— = —CMe₂—; R¹ = 4-MeOC₆H₄;
R² = Me, 4-MeOC₆H₄; R³ = H, Me;
—Y— = —CH₂CH(OH)CH₂OR⁴OCH₂CH(OH)CH₂—;
—R⁴— = ,
—(CH₂)₄—, .

The majority of studies in this field deal with polymers in which the NBD residues are 'attached' to the main chain of the macromolecule.[5,94–103] For example, polyisoprene **51** is isomerised in a benzene solution in the presence of $(PPh_3)_2CuBr$ as the sensitiser.[94] The reaction **52** → **51** is thermally reversible on heating of the polymer to 180 °C.

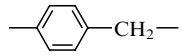


51 ⇌ **52**

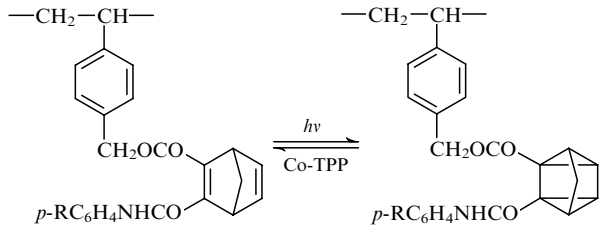
Irradiation of polymers **53**, which contain the residue of 3-phenylnorbornadiene-2-carboxylic acid, with light with $\lambda_{irr} = 313$ nm results in their isomerisation into quadricyclanes **54**.[95,96] The reverse transformation is performed upon irradiation at $\lambda_{irr} = 248$ nm, heating to 100 °C, or adding Co-TPP to a solution of the polymer **54** in dichloromethane.



53 ⇌ **54**

—X— = , —O—(CH₂)₂—.

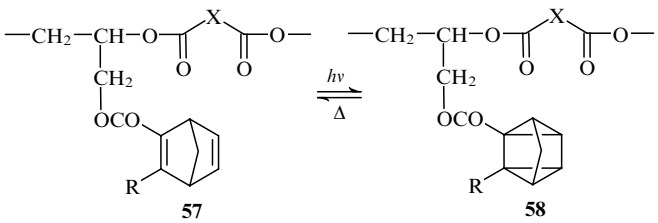
Polymer-bound amides **55a–e** were obtained in order to shift λ_{ae} to higher wavelengths; they are characterised by absorption at $\lambda_{max} = 323–351$ nm and an absorption edge at $\lambda_{ae} = 425–440$ nm.[97] Under irradiation of compounds **55a–e** with light of a mercury lamp or with sunlight, the valence isomerisation occurs readily, both in solid phase and in solutions of the polymers in THF. Its efficiency increases in the series: **55e** < **55d** ⩽ **55a** < **55b** < **55c**. Addition of Co-TPP to solutions of the quadricyclanes **56a–e** at 298 K results in their isomerisation into norbornadienes **55a–e** with a rate constant $k = (0.5–0.7) \times 10^3$ s^{-1}. The amount of the accumulated solar energy is evaluated to be 60 kJ mol^{-1}, although the presence of an *N*,*N*-disubstituted amide group in the norbornadiene fragment increases it to 80–86 kJ mol^{-1} (see Ref. 98).



55a–e ⇌ **56a–e**

R = H (**a**), Me (**b**), OMe (**c**), Cl (**d**), COMe (**e**).

Binding of NBD moieties with a polyester macromolecule gave photoactive systems **57**.[5] Valence isomerisation of the latter into quadricyclanes **58** occurs readily under irradiation of the polymer at $\lambda_{irr} \leqslant 400$ nm, both in solid phase and in solutions in THF ($\Phi = 0.33–0.41$). The reverse transformation **58** → **57** is carried out using low-temperature initiation (62–75 °C). The amount of solar energy accumulated in this photoreaction is very high, *viz.*, about 90 kJ mol^{-1}.

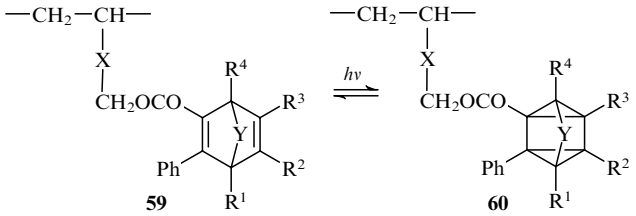


57 ⇌ **58**

—X— = —C₆H₄—, —(CH₂)₂—, , ;
R = Ph, CONPr₂, CO₂Me.

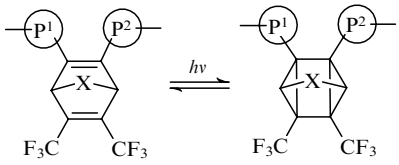
Polymers **59** with the residues of 'donor–acceptor' NBD were obtained in order to shift the λ_{ae} values farther towards the solar radiation maximum.[99] However, they were found to have $\lambda_{ae} \leqslant 350$ nm. Nevertheless, these compounds are characterised

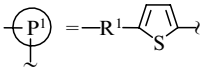
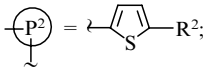
by high turnover rate of the **59** ⇋ **60** transformation and can store 55–74 kJ mol^{-1} of thermal energy.

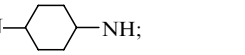


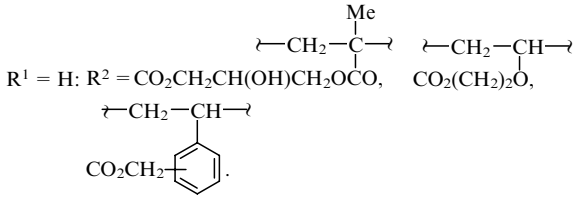
—X— = —C_6H_4—, —OCH_2—; —Y— = —CH_2—, —CHMe—; $R^1 = R^2 = R^3 = R^4$ = H, Me.

Polymers **61** containing trifluoromethyl-substituted NBD present an improved version of systems of this type. Their efficient phototransformation into the isomers **62** can be carried out under irradiation in the visible spectral region (up to $\lambda_{ae} \leqslant 505$ nm).[100]

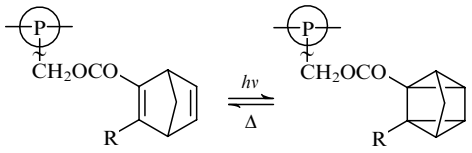


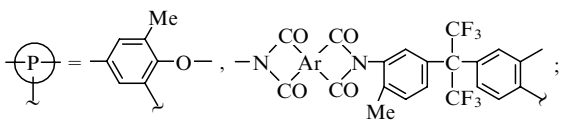
X = CMe_2;  ; ;

R^1 = CO: R^2 = $CO(CH_2)_6O$–, ;



The main drawback of the majority of the polymeric systems described above is their insufficient photo- and thermal stability, which limits the NBD ⇋ Q turnover number. When norbornadienes **63** bound to a rigid polymeric system undergo photoisomerisation, they maintain the most important spectral and photochemical features of the NBD → Q transformation, but they have an enhanced stability in the cyclic reactions **63** ⇋ **64**.[101, 102]





R = Ph, CONHAr.

Norbornadiene-containing polystyrenes insoluble in organic solvents are even more stable.[103] Irradiation of their suspensions in dichloromethane results in isomeric quadricyclanes; in the presence of Co-TPP, the reverse reaction occurs with liberation of accumulated energy (44–77 kJ mol^{-1}).

VI. Conclusion

Analysis of recently published studies on the valence isomerisation of norbornadiene and its derivatives into the corresponding quadricyclanes revealed two major trends in relation to the accumulation of solar energy: (1) the total number of publications on this subject has decreased somewhat; (2) at the same time, we observe a significant increase in the number of studies that not only pose a certain problem but also suggest specific ways to solve it practically. In our opinion, this indicates that this problem is nearly solved rather than that the interest in the accumulation of solar energy with the use of NBD is being lost. As mentioned previously,[1] the thermal energy obtained by the method in question is more expensive than that generated by conventional methods, but cost issues will inevitably become less important as natural fuel resources are exhausted. We distinguished four main competing approaches that are used for enhancing the efficiency of isomerisation of norbornadienes into quadricyclanes. It can be concluded that considerable success has been reached along each of these directions. Efficient ways for the photosensitisation of this reaction have been developed using metal complexes or sensitisers chemically bound with the NBD molecule; in certain cases, the number of working cycles can be as high as 5000. Owing to the enhanced thermal stabilities of 'donor–acceptor' systems in which NBD molecules contain perfluoroalkyl substituents, such derivatives are promising for practical application. 2,3-Disubstituted NBD are serious competitors to these systems. This is primarily due to the facts that they are easier to synthesise and that they can absorb sunlight in the spectral region $\lambda > 400$ nm. Polymer-bound NBD can provide acceptable cyclicity and allow up to 94 kJ mol^{-1} of solar energy to be accumulated. It is also obvious that, beside the accumulation of solar energy, the norbornadiene–quadricyclane system finds diverse new fields of application: creating molecular switches[61, 104, 105] and optical waveguides on their basis,[106, 107] developing new types of photochromic chemosensors for metal cations[108, 109] and photo-switchable organic magnetic materials.[110–112] Furthermore, NBD-containing polymers can be used as energy-boosting additives for rocket fuel.[94]

This review was financially supported by the Russian Foundation for Basic Research (Project Nos 02-03-32527 and 00-15-97320) and the Civilian Research and Development Foundation (CRDF)–at the Russian Federation Ministry for Education (Grant No. REC-004).

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