Electron-Transfer Photochemistry of Benzocyclobutenes Stereospecific Electrocyclic Reactions of their Cation Radicals

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The facile activation of *cis*- and *trans*-1,2-diphenylbenzocyclobutene (DBC) either by charge-transfer irradiation of the electron donor-acceptor complex with tetracyanoethylene or by chloranil photosensitization leads to a series of rapid [4 + 2] cycloadditions. The role of the cation radical $DBC^{+\cdot}$ as the reactive intermediate which undergoes a stereospecific, conrotatory cycloreversion is delineated, especially with regard to "contact" and "solvent-separated" ion pairs. Such cycloadditions induced by electron transfer are discussed in the context of the thermal valence tautomerization of DBC previously established by Huisgen, Quinkert, and co-workers.

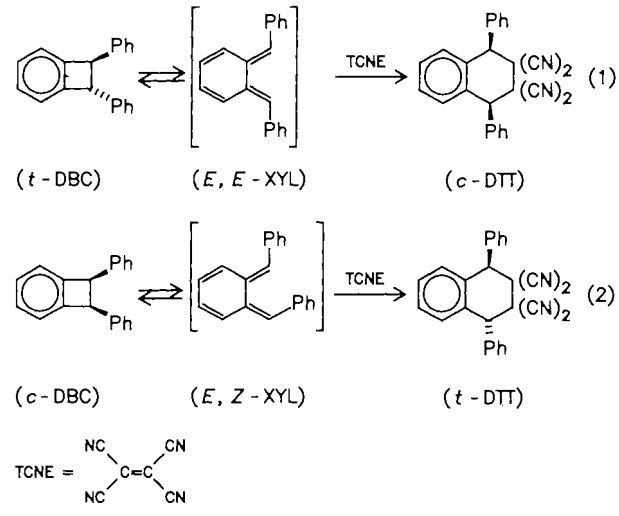
Elektron-Transfer-Photochemie von Benzocyclobutenen. – Stereospezifische elektrocyclische Reaktionen ihrer Kation-Radikale

Die leichte Aktivierung von *cis*- und *trans*-1,2-Diphenylbenzocyclobuten (DBC) entweder durch Bestrahlung der Charge-transfer-Verbindung mit Tetracyanethylen oder durch Photosensibilisierung mit Chloranil führt zu einer Serie schneller [4 + 2]-Cycloadditionen. Die Rolle des Kationradikals $DBC^{+\cdot}$ als reaktives Zwischenprodukt, das eine stereospezifische conrotatorische Cycloreversion eingeht, wird vorwiegend über „Kontakt"- oder „Lösungsmittel-getrennte" Ionen-Paare erklärt. Solche Cycloadditionen, die durch einen Elektronentransfer eingeleitet werden, werden im Zusammenhang mit einer thermischen Valenztautomerie von DBC diskutiert, wie sie früher von Huisgen, Quinkert und Mitarbeitern begründet wurden.

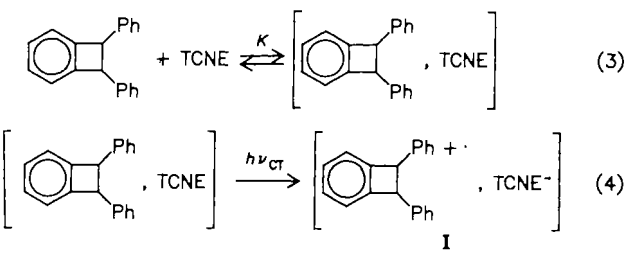
Electron donor-acceptor (EDA) interactions play an important role in organic chemistry, and both stable as well as transient EDA complexes have been observed with a wide variety of organic donors (D) and acceptors (A)[1]. Especially relevant is the role of ground state [D,A] and ionic $[D^{+\cdot}, A^{-\cdot}]$ complexes in thermal and photochemical electrocyclic processes[2,3]. For example, thermal [2 + 2] cycloadditions and Diels-Alder condensations can involve strong electron donor-acceptor interactions[4,5], and photo [2 + 2] cycloadditions can be facilitated via exciplexes[6]. Morever, the microscopic reverse, e.g., cycloreversion can also be induced by EDA interactions[7]. Indeed the symmetry "forbidden" aromatization of hexamethyl Dewar benzene is a particularly interesting example of such an electrocyclic process which is induced by photosensitization[8], charge-transfer excitation[9], or ground-state EDA catalysis[10]. Metal ions such as silver(I) and rhodium(I) have also been used for the efficient catalysis of ring opening to hexamethylbenzene[11]. These diverse observations pose an interesting question as to whether EDA interactions are effective in symmetric "forbidden" as well as "allowed" processes. Hexamethyl Dewar benzene is not a suitable substrate to address this point since it must perforce undergo aromatization by electrocyclic ring opening in a disrotatory manner. Accordingly we sought a system which is not so constrained in order to examine the electrocyclic stereochemistry stemming from EDA interactions. One such system is benzocyclobutene[12,13] particularly the *cis*- and *trans*-1,2-diphenyl analogues which Huisgen, Quinkert, and co-workers have concluded undergo a conrotatory ring opening on the basis of stereospecific formation of Diels-Alder adducts, e.g.[14,15].

Most relevant to our studies was the qualitative observation of transient yellow colors which were gradually bleached as the cycloadditions progressed[15,16]. Such colors are commonly associated with complexes of organic donors and the tetracyanoethylene (TCNE) acceptor[1], and they are derived from the charge-transfer (CT) excitation of the EDA complex to the ion-pair state **I**, e.g. ref.[17].

The ion-pair state **I** in eq. 4 represents the extremum of an EDA interaction in which the benzocyclobutene donor has been converted to its radical cation.



Scheme 1



In this study we focus on three interrelated aspects of the benzocyclobutene cation radical.

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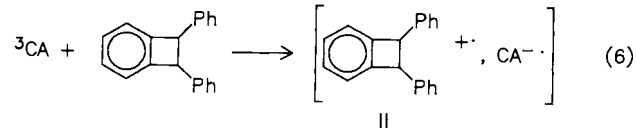
(A). We initially inquire as to whether the radical-ion pair **I** in Scheme 1 will lead to the Diels-Alder adducts in eqs. 1 and 2; and if so, with what stereochemistry.

(B). Ion pairs similar to **I** can also be generated by the diffusional quenching of an excited acceptor such as chloranil (CA),[18,19] see Scheme 2.

Scheme 2

$$CA \xrightarrow{h\nu} {}^1CA^* \xrightarrow[(fast)]{isc} {}^3CA \qquad (5)$$



(6)

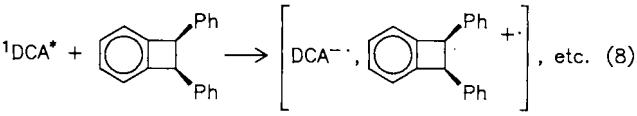
II

The possibility of cycloadduct formation from reactive intermediates such as **II** then raises questions similar to those posed by **I**.

(C). Finally the behavior of benzocyclobutene cation radical can be examined by the photo-sensitized reaction involving the singlet-excited state of 9,10-dicyanoanthracene (DCA)[20,21], Scheme 3.

Scheme 3

$$DCA \xrightarrow{h\nu} {}^1DCA^* \qquad (7)$$



(8)

III

Although dicyanoanthracene is not a viable acceptor ($E_{1/2} = -0.98$ V vs SCE), the excited singlet state in eq. 7 is calculated to have an oxidation potential of $E_{1/2} \approx +1.9$ V. Thus the formation of the benzocyclobutene cation radical by electron transfer in eq. 8 is expected to be favorable[22].

In the following, we first present spectral evidence for the electron donor-acceptor interactions of benzocyclobutenes with electron acceptors such as tetracyanoethylene (see eq. 3). This is followed by the three approaches to photoinduced electron transfer as described in Schemes 1, 2, and 3, especially with regard to the chemical consequences attendant upon the formation of benzocyclobutene cation radicals in cycloaddition reactions.

Results

I. Charge-Transfer Spectra of Benzocyclobutenes with Tetracyanoethylene. Formation of the Electron Donor-Acceptor Complex

When a solution of either *cis*- or *trans*-1,2-diphenylbenzocyclobutene was mixed with tetracyanoethylene, an immediate yellow-red coloration developed. The absorption bands accompanying this spectral change are shown in Figure 1. Since neither the benzocyclobutene nor tetracyanoethylene absorbed in the visible region, the broad absorption band was readily assigned to the intermolecular electron donor-acceptor complex (see eq. 3), which is similar to that of other EDA complexes from various aromatic donors with tetracyanoethylene[23].

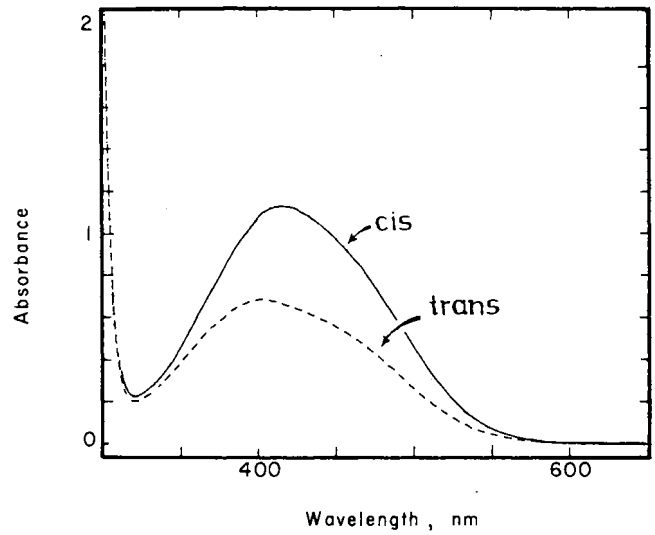


Figure 1. Charge-transfer absorption band of the electron donor-acceptor complex of tetracyanoethylene ($5.0 \cdot 10^{-2}$ M) with *cis*- and *trans*-1,2-diphenylbenzocyclobutene ($2.5 \cdot 10^{-2}$ M) in dichloromethane

The formation constants K of the EDA complexes of TCNE with *cis*- and *trans*-1,2-diphenylbenzocyclobutene were measured spectrophotometrically by the Benesi-Hildebrand procedure[24,25]. Thus for the 1:1 complex in eq. 3, the change in the absorbance A_{CT} of the charge-transfer band at λ_{max} with the variation in the concentration of the diphenylbenzocyclobutene [DBC] and [TCNE] is given by eq. 9

$$\frac{[TCNE]}{A_{CT}} = \frac{1}{\varepsilon_{CT}} + \frac{1}{K\varepsilon_{CT}[DBC]} \qquad (9)$$

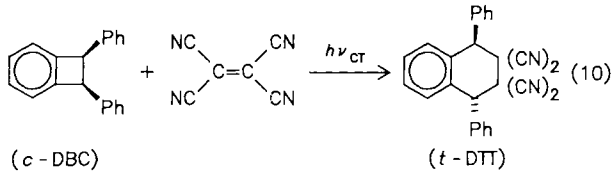
under conditions in which [TCNE] $\ll$ [DBC]. The values of K for *cis*- and *trans*-1,2-diphenylbenzocyclobutene obtained with the aid of eq. 9 (see Experimental) were 0.87 and 1.6 M^{-1}, respectively, with a correlation coefficient $r = 0.999$. The molar extinction coefficients for the EDA complexes obtained from *cis*- and *trans*-diphenylbenzocyclobutenes were 1130 and 390 M^{-1} cm^{-1} at the absorption maxima $\lambda_{CT} = 416$ and 404 nm, respectively. The limited magnitudes of the formation constant of both the *cis*- and *trans*-isomers indicated that these intermolecular EDA complexes are best classified as weak. Furthermore, the limited variation in the magnitudes of λ_{CT}, K or ε_{CT} obtained from *cis*- and *trans*-diphenylbenzocyclobutene indicated that the EDA complexes derived from these isomers were not qualitatively distinguishable.

A careful examination of Figure 1 shows that both of the charge-transfer absorption bands of the TCNE complexes with diphenylbenzocyclobutene are unsymmetric, with barely perceptible shoulders at $\approx$ 450 and 470 nm for the

trans- and *cis*-isomer, respectively. Attempts to more clearly resolve these bands in other solvents or by concentration variation were unsuccessful. Multiple CT bands have been observed in TCNE complexes with alkylaromatics[17,26], and can be assigned to CT transitions from the highest occupied molecular orbital (HOMO) and the subjacent orbital (SHOMO) arising from the removal of the degeneracy of the $^2E_{1g}$ level of benzene by substitution[27]. As applied to the isomeric diphenylbenzocyclobutenes, we tentatively assign the low energy band at $\approx$ 430 nm to transitions from the HOMO centered about the benzocyclobutene moiety. The high energy maximum at $\approx$ 405 nm corresponds to that of the toluene (λ_{max} = 408 nm) and bibenzyl (λ_{max} = 412 nm) complex. For comparison, the CT band of the TCNE complex with benzocyclobutene occurs at λ_{max} = 424 nm[28,31].

II. Charge-Transfer Excitation of the EDA Complexes of *cis*- and *trans*-1,2-Diphenylbenzocyclobutene and Tetracyanoethylene

When a dichloromethane solution containing $2.5 \cdot 10^{-2}$ M *cis*-1,2-diphenylbenzocyclobutene (*c*-DBC) and $5.0 \cdot 10^{-2}$ M tetracyanoethylene at 25°C was irradiated at wavelengths > 380 nm, the yellow-red color was bleached within 20 min. ^{1}H-NMR analysis of the photolysate followed by isolation of crystalline *trans*-1,4-diphenyl-2,2,3,3-tetracyanotetralin (*t*-DTT) in 90% yield established the stoichiometry of the photochemical process to be cleanly as in eq. 10.



From the absorption spectrum in Figure 1 we concluded that the actinic radiation at λ > 380 nm could excite only the charge-transfer band of the EDA complex. Thus there was no ambiguity about either the adventitious local excitation of the complexed (or uncomplexed) chromophores or the generation of intermediates which did not arise from the CT excitation of the EDA complex. The photo-induced cycloaddition in eq. 10 must, therefore, have been a direct consequence of the population of the CT-excited state.

Similarly, the CT irradiation at λ > 380 nm of a dichloromethane solution containing $2.5 \cdot 10^{-2}$ M of the isomeric *trans*-diphenylbenzocyclobutene and $5.0 \cdot 10^{-2}$ M tetracyanoethylene led to the same bleaching of the yellow-red solution within 20 min. ^{1}H-NMR analysis of the photolysate followed by isolation of the crystalline *cis*-diphenyltetracyanotetralin (*c*-DTT) as the sole isomer in 70% yield (see Table 1), established the stoichiometry of the photochemical process to be cleanly according to eq. 11.

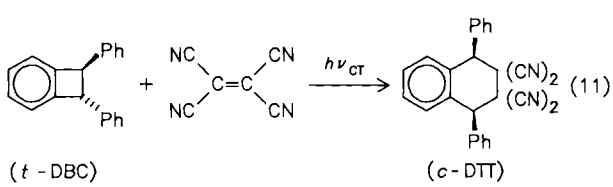


Table 1. CT-Induced cycloaddition of 1,2-diphenylbenzocyclobutenes (DBCs) to tetracyanoethylene[a]

DBC	Solvent	Conditions[b]	Time (h)	Product (%)	Recovery[c] (%)
trans	CH_2Cl_2	Δ	20	*c*-DTT (98)	-
			3	*c*-DTT (90)	6
			0.5	*c*-DTT (23)	77
trans	CH_2Cl_2	*hν*	0.3	*c*-DTT (70)	28
cis	CH_2Cl_2	Δ	96	*t*-DTT (24)	76
			48	*t*-DTT (12)	88
cis	CH_2Cl_2	*hν*	0.3	*t*-DTT (90)	5
cis	MeCN	Δ	96	*t*-DTT (25)	73
cis	MeCN	*hν*	0.3	*t*-DTT (44)[d]	45
cis	CH_2Cl_2/MeOH[e]	*hν*	0.2	*t*-DTT (69)	25
cis	MeCN/MeOH[e]	*hν*	0.2	*t*-DTT (18)	75

[a] In solutions containing 0.050 mmol of DBC and 0.10 mmol of TCNE in 2 ml of solvent at 24°C. — [b] in the dark; *hν* = actinic irradiation with λ > 380 nm (see Experimental). — [c] Of reactant in the reaction mixture. — [d] In addition to 2% (0.001 mmol) of *c*-DTT. — [e] Presence of MeOH led to new absorptions at 420 nm.

^{1}H-NMR analysis showed that none of the *trans*-isomer (< 1%) was present in the mixture according to eq. 11 and similarly *c*-DTT (< 1%) was absent after reacting according to eq. 10. However when the CT irradiation of *c*-DBC was carried out in acetonitrile, the conversion to the cycloadduct *t*-DTT was diminished by $\approx$ 50%, and a small but discrete amount of the isomeric *cis*-adduct *c*-DTT was observed in the ^{1}H-NMR analysis.

The molecular structures of the cycloadducts *t*- and *c*-DTT formed in eqs. 10 and 11, respectively, were determined by comparison with those established earlier by Huisgen, Quinkert, and co-workers[14-16]. Thus the cycloadduct *t*-DTT was identical with the Diels-Alder adduct obtained from the thermal reaction of *cis*-1,2-diphenylbenzocyclobutene with tetracyanoethylene in the same solvent (see Table 1). Similarly the cycloadduct *c*-DTT was identical with that obtained from *trans*-1,2-diphenylbenzocyclobutene under identical conditions. The earlier studies of Huisgen, Quinkert, and co-workers established both of these cycloadducts to arise by the stereospecific conrotatory opening of the benzocyclobutene ring (see eqs. 1 and 2)[14-16]. Therefore the difference between the photochemical and thermal processes lay in the time required for the cycloaddition to occur. For example, the thermal reaction of *cis*-diphenylbenzocyclobutene with TCNE was slow, and within a 24-h span it proceeded to only 7% conversion in the dark at 25°C. At this temperatures, the corresponding thermal reaction of the *trans*-isomer with TCNE occurred somewhat more rapidly[32]. However the rates of the photochemical and thermal processes were greatly differentiated at lower temperatures. Thus the rate of the photochemical process was essentially unaffected at −46°C, and the contribution from the thermal process could be reduced to less than 5% at this temperature (see Experimental).

III. Quantum Yield for the CT-Induced Cycloaddition of Benzocyclobutene to Tetracyanoethylene

Owing to the multiple CT transitions which appear in Figure 1, we examined the wavelength dependence of the

quantum yield for the photo-induced cycloaddition of TCNE to *cis*-1,2-diphenylbenzocyclobutene (in which there exists no ambiguity about competition from the thermal process). The series of excitation energies listed in Table 2 encompass the entire CT band from the high energy edge (366 nm) to the low energy tail (480 nm). The efficiencies were based on Reinecke salt actinometry[33,34] at low conversion (5–10%) using monochromatic light provided by a series of interference filters. The absence of significant differences in the quantum yield in Table 2 could be due to the severe overlapping of the multiple CT bands.

Table 2. Wavelength dependence of the CT cycloaddition of *cis*-1,2-diphenylbenzocyclobutene (*c*-DBC) and TCNE[a]

	Excitation Wavelength (nm)			
	366	405	436	480
Φ	0.31	0.34	0.36	0.34
			0.34	0.35

[a] With 0.050 mmol of *c*-DBC and 0.10 mmol of TCNE in 2 ml of dichloromethane at 24°C.

The maximum of the CT absorption band of the TCNE complex of *cis*-diphenylbenzocyclobutene varied somewhat with the solvent polarity, as shown in Table 3. The solvent effect on the course of photochemistry was measured by following the absorbance change at the maximum of the charge-transfer absorption band at a constant excitation energy. The quantum yields in Table 3 were all obtained at photochemical conversions of less than 5%. The results in Table 3 show that there is a slight trend for the quantum efficiency of the photo-induced cycloaddition to increase in tetrachloromethane. The latter, however, may be an artifact of the lower concentrations of TCNE owing to its limited solubility in this nonpolar medium.

Table 3. Solvent effect on quantum yield of the CT-induced cycloaddition of *cis*-1,2-diphenylbenzocyclobutene and tetracyanoethylene[a]

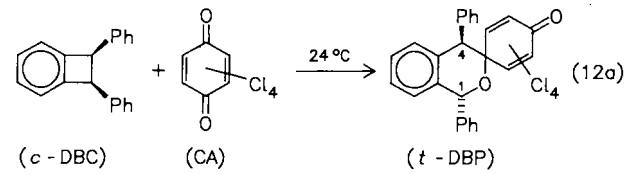
Solvent	λ_{CT}[b]	Φ[c]
CCl_4[d]	422	0.66
CH_2Cl_2	416	0.34
CH_3CO_2Et	385	0.32, 0.35

[a] With 0.50 mmol of benzocyclobutene and 0.10 mmol of TCNE in 2 ml of solvent at 25°C, unless indicated otherwise. – [b] Absorption maximum. – [c] Irradiation at 405 nm, conversion 5–10%. – [d] Owing to limited solubility [TCNE] = $3.44 \cdot 10^{-3}$ mmol.

IV. Cycloadditions of 1,2-Diphenylbenzocyclobutenes to Chloranil

The behavior of the electron acceptor chloranil (CA) was similar to that of TCNE in that it reacted with the diphenylbenzocyclobutenes both thermally and under actinic stimulation, as described separately below.

(A). *Thermal* reactions of *cis*-diphenylbenzocyclobutene with 1 equiv. of chloranil proceeded slowly at 24°C in dichloromethane to afford a single adduct *t*-DBP in 22% yield after 96 h. (The unreacted *c*-DBC was recovered in 75% yield.) The presence of a broad absorption at ≈ 310 nm in the UV-VIS spectrum of *t*-DBP was characteristic of a cyclohexadienone moiety. Indeed the successful growth of a single crystal of *t*-DBP allowed its structure to be established by X-ray crystallography. The ORTEP diagram of *t*-DBP in Figure 2 shows it to have the *trans*-diphenylbenzopyran structure in which the stereospecific addition of *c*-DBC to chloranil has occurred across the carbonyl group in a 1:1 stoichiometry, eq. 12a.



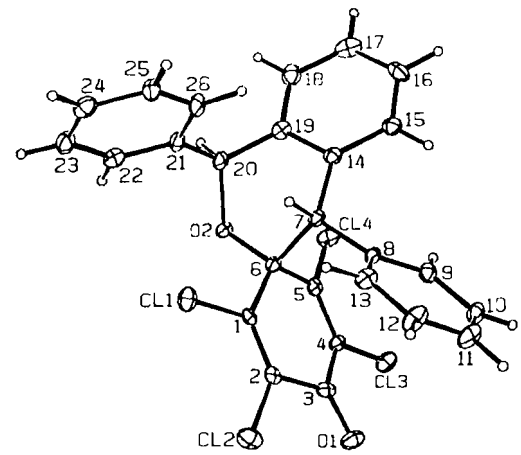
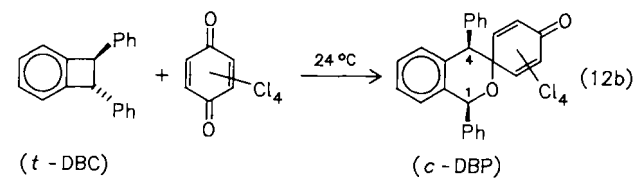


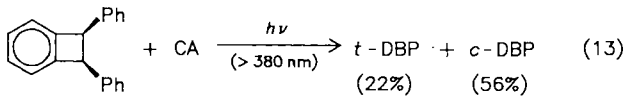
Figure 2. ORTEP diagram of the cycloadduct *t*-DBP from *cis*-1,2-diphenylbenzocyclobutene and chloranil showing the *trans*-phenyl substituents and the benzodihydropyran backbone

The pair of singlet resonances at δ 5.02 and 6.58 in the ^{1}H-NMR spectrum of *t*-DBP in dichloromethane was readily assigned to the unique tertiary hydrogens at C-1 and C-4, respectively. None of the isomeric *cis*-cycloadduct (vide infra) was detected. Treatment of the *trans*-benzocyclobutene *t*-DBC with 1 equiv. of chloranil under the same conditions also afforded at 24°C a single adduct *c*-DBP in 87% yield after only 6 h. The infrared and UV-VIS spectra of *c*-DBP were essentially the same as those of *t*-DBP (see Experimental), and the ^{1}H-NMR spectrum showed the presence of a pair of tertiary hydrogens at δ 5.03 and 6.26[35]. These spectroscopic results coupled with a confirmatory elemental analysis (see Experimental) supported the formation of an isomeric 1:1 adduct with *cis* stereochemistry at C-1 and C-4.



None of the *trans*-cycloadduct formed in eq. 12a from the *cis*-diphenylbenzocyclobutene was found. Accordingly, it is important to note that the stereospecific cycloaddition of chloranil to *cis*- and *trans*-diphenylbenzocyclobutene as represented in eq. 12a/b proceeds in the same sense as that previously observed with tetracyanoethylene (see Scheme 1)[14–16].

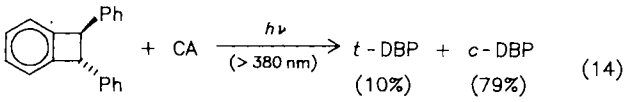
(B) The *photostimulated* reaction of $5 \cdot 10^{-3}$ M diphenylbenzocyclobutene with 2 equiv. of chloranil (CA) was carried out at 24°C in dichloromethane at wavelengths $\lambda > 380$ nm by passing the output from a 1 kW Hg-Xe lamp through a Corning sharp cutoff filter. Under these conditions *cis*-diphenylbenzocyclobutene was 90% converted within 3 min to a mixture of 1:1 cycloadducts described in eq. 12a/b, viz., 22% *t*-DBP and 56% *c*-DBP. No other products were detected.



(13)

(*c*-DBC)

Moreover, the irradiation of a solution of chloranil and the isomeric *trans*-diphenylbenzocyclobutene under the same conditions led to a 97% conversion of the donor within 3 min to afford a mixture of 1:1 cycloadducts, eq. 14.



(14)

(*t*-DBC)

The photosensitized addition of *cis*- and *trans*-diphenylbenzocyclobutene to chloranil thus clearly shows no stereospecificity, unlike the thermal counterparts in eq. 12a/b. Furthermore the quenching of chloranil was not dependent on the donor, since the quantum yields Φ measured at various concentrations of diphenylbenzocyclobutene, as given in Table 4, were invariant within experimental error.

Table 4. Concentration dependence of the quantum yield for the photosensitized cycloaddition of *cis*-diphenylbenzocyclobutene to chloranil[a]

c-DBC (M)	Φ[b]
$5.00 \cdot 10^{-3}$	0.86
$7.53 \cdot 10^{-3}$	0.82
$9.99 \cdot 10^{-3}$	0.85
$1.33 \cdot 10^{-2}$	0.82
$2.01 \cdot 10^{-2}$	0.81

[a] In 2 ml of dichloromethane containing $1.0 \cdot 10^{-2}$ M chloranil and variable amounts of *c*-DBC by passing the output from a 1-kW Hg–Xe lamp through a Corning 380-nm cutoff filter and an Edmund 405-nm ± 5 nm interference filter. — [b] Based on decrease in chloranil absorbance $\varepsilon = 235\ M^{-1}\ cm^{-1}$ at 376 nm, which was measured spectrophotometrically after dilution of the photolyzed solution.

Table 5. Charge-transfer absorption spectra of aromatic complexes with chloranil[a]

Arene	IP (eV)[b]	λ_{CT} (nm)[c]	ν_{CT} (cm^{-1})
Hexamethylbenzene	7.85	520	19.2
Durene	8.05	480	20.8
o-Xylene	8.56	406[d]	24.6
Toluene	8.92	366[d]	27.3
Benzocyclobutene	8.66[f]	~ 390[e]	~ 26

[a] In dichloromethane solution containing $1 \cdot 10^{-3}$ M chloranil and 0.1 – 1.0 M arene. — [b] Ref.[22]. — [c] At experimental maximum, unless indicated otherwise. — [d] Estimated from difference spectra. — [e] Interpolated value. — [f] From ref.[30].

It is important to establish that actinic irradiation of a solution of chloranil and diphenylbenzocyclobutene led primarily to the electronic excitation of chloranil according to Scheme 2 and not the EDA complex (compare Scheme 1). In order to locate the CT-absorption bands of the CA complex of diphenylbenzocyclobutene, we examined the series of methylbenzene donors in Figure 3. The CT bands of hexamethylbenzene ($\lambda_{CT} = 520$ nm) and durene ($\lambda_{CT} = 480$ nm) with chloranil were clearly resolved from the local ($n \rightarrow \pi^*$) excitation of chloranil ($\lambda_{max} = 376$ nm), but that of *o*-

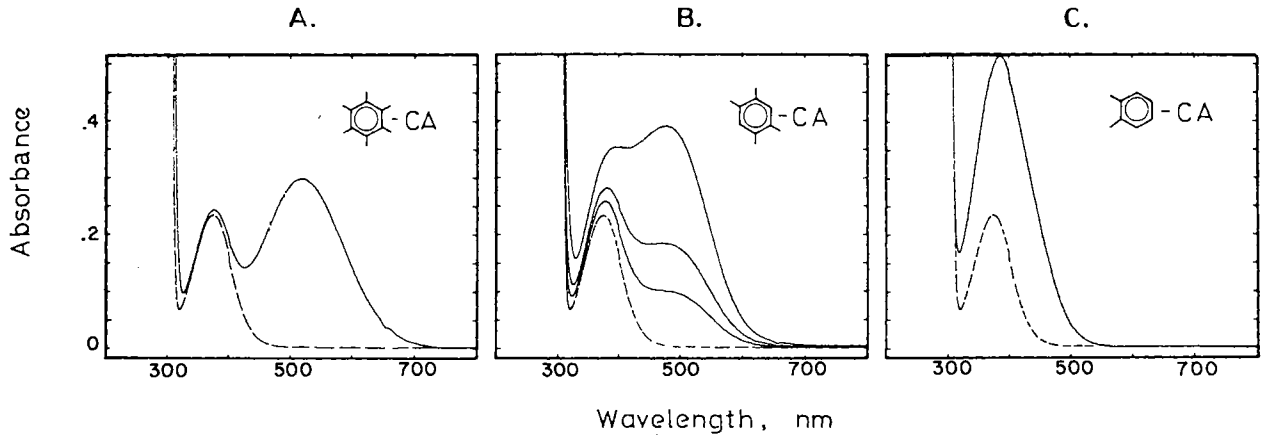


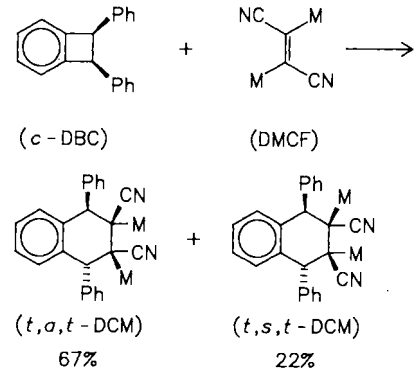
Figure 3. CT absorption spectra derived from the EDA complexes of $1.0 \cdot 10^{-3}$ M chloranil with (A) $5.0 \cdot 10^{-2}$ M hexamethylbenzene, (B) $5.0 \cdot 10^{-2}$, and 0.1, 0.25 M durene, and (C) 0.85 M *o*-xylene in dichloromethane. The spectrum of $1.0 \cdot 10^{-3}$ M chloranil is shown by dashed line

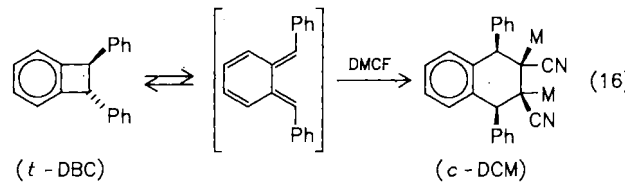
xylene was not (Figure 3C). We conclude from the trend in the CT bands with the ionization potentials shown in Table 5 that the absorptions of the EDA complexes of *o*-xylene and benzocyclobutene indeed overlap with the chloranil absorption. However the more than hundred-fold higher absorbance of chloranil compared to that of the EDA complex at the relevant concentrations employed in this study[36] ensures that only the local excitation of chloranil is significant for irradiations at $\lambda > 380$ nm.

V. Trapping of Intermediates in the Photosensitized Cycloaddition of 1,2-Diphenylbenzocyclobutene to Chloranil

The lack of stereospecificity in the photosensitized cycloaddition of chloranil to diphenylbenzocyclobutene suggested the interception possibly of a transient intermediate. Two dienophiles were used as traps for this purpose, dimethyl dicyanofumarate and tetracyanoethylene since neither of these electron acceptors absorbs actinic light at $\lambda > 380$ nm[37].

(A) *Dimethyl dicyanofumarate* (DMCF) was examined as a dienophilic trap by first identifying its thermal cycloadducts with diphenylbenzocyclobutenes. Thus treatment of DMCF with *cis*-1,2-diphenylbenzocyclobutene at 75°C for 3 hours afforded a pair of isomeric 1:1 adducts as judged by the presence of two different methoxy resonances at δ 3.54 and 3.60 and two different methine protons at δ 5.51 and 5.40 both in 3:7 intensity ratios in the ^{1}H-NMR spectrum of the reaction mixture. Chromatographic separation yielded the minor isomer in 22% yield. The major cycloadduct was isolated in 67% yield, and a single crystal suitable for X-ray crystallography was successfully grown. The ORTEP diagram in Figure 4 shows the structure of the cycloadduct *t,a,t*-DCM in which the pair of phenyl groups are *trans*, the phenyl and methoxycarbonyl groups are *anti*, and the pair of cyano groups are *trans*. The minor cycloadduct was then assigned as the *trans, syn, trans*-isomer on the basis of spectral analysis (see Experimental), eq. (15), where M = methoxycarbonyl. [Note these isomers correspond to the *endo*- and *exo*-additions of dimethyl dicyanofumarate to (*E,Z*)-diphenyl-*o*-xylylene (compare eq. 2).] A similar treatment of the *trans*-diphenylbenzocyclobutene with DMCF at 24°C yielded a single 1:1 adduct in 97% yield after 6 hours. Its spectral similarity to those of the isomeric DMCF adducts in eq. 15 (see Experimental) together with the analogy to eq. 1 suggested the formation of the *cis*-diphenyl adduct according to eq. 16.





The reactivity of dimethyl dicyanofumarate relative to chloranil was determined by the competition method. For example, when a 1:5 molar ratio of CA:DCM was treated with a limited amount of *cis*-diphenylbenzocyclobutene, the relative amounts of the cycloadducts DPB:DCM were 1:1, as listed in entries 1 and 2, Table 6. The isomeric *trans*-diphenylbenzocyclobutene under comparable conditions led to a 2.6:1 ratio of DPB:DCM adducts from chloranil and dimethyl dicyanofumarate, respectively. Otherwise the mixture of cycloadducts corresponded to the superposition of those adducts obtained stereospecifically in the individual thermal reactions in eq. 12a/b and 15/16. In the photosensitized process, the competition from the foreign dienophile (DMCF) was informative in three ways. First, the quenching of the excited chloranil by diphenylbenzocyclobutene did not yield only DBP adducts as described in eq. 13/14, but also adducts derived from the dienophilic trap DMCF[37]. Second, compared to the thermal competition (entries 1–3, Table 6) the photosensitized process yielded a mixture of cycloadducts (entries 4 and 5) which consisted of a higher molar fraction derived from chloranil – the ratio DPB:DCM being 3.8:1 with *cis*-diphenylbenzocyclobutene

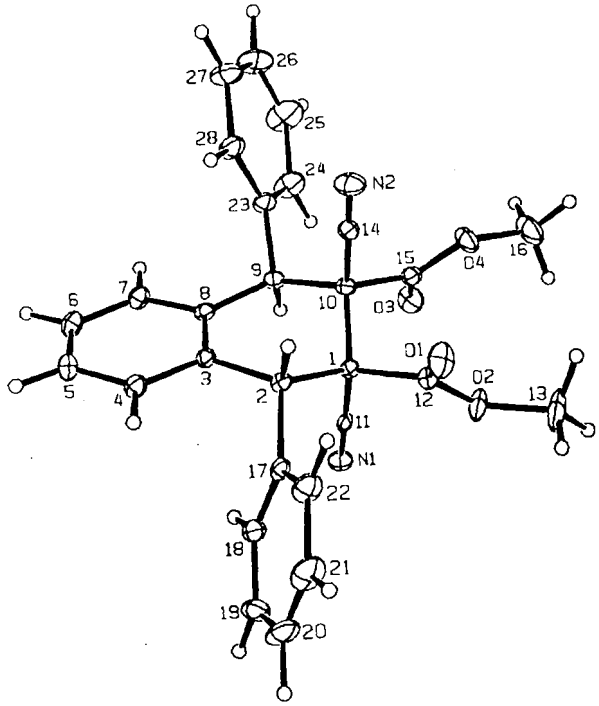


Figure 4. ORTEP diagram of the cycloadduct *t,a,t*-DCM from *cis*-1,2-diphenylbenzocylobutene and dimethyl dicyanofumarate showing the *trans*-diphenyl,*anti*-phenyl ester and *trans*-dicyano groups

Table 6. Effect of dimethyl dicyanofumarate (DMCF) on the thermal and photosensitized cycloaddition of diphenylbenzocyclobutenes (DBC) to chloranil

Donor (mmol)	Chloranil (mmol)	Dienophile (mmol)	Conditions[a]	Cycloadducts (%)[b]
c-DBC (0.025)	(0.050)	DMCF (0.25)	Δ(250, 24) CH_2Cl_2(5 mL)	t-DBP, tat-DCM, tst-DCM (25) (17) (6)
c-DBC (0.025)	(0.050)	DMCF (0.25)	Δ(3,reflux) MeCN(5 mL)	t-DBP, tat-DCN, tst-DCM (44) (32) (18)
t-DBC (0.050)	(0.10)	DMCF (0.50)	Δ(6, 24) CH_2Cl_2(10 mL)	c-DBP, c-DCM (64) (25)
c-DBC (0.025)	(0.050)	DMCF (0.25)	hν CH_2Cl_2(5 mL)	t-DBP, c-DBP, (7) (52); tat-DCM, tst-DCM, c-DCM (4) (2) (10)
t-DBC (0.025)	(0.050)	(0.25)	hν CH_2Cl_2(5 mL)	t-DBP, c-DBP, (1) (64); tat-DCM, tst-DCM, c-DCM (5) (2) (16)

[a] Δ = thermal reaction in the dark (duration in h, temperature in °C). hν = actinic irradiation for 3 min at 24°C and λ > 380 nm. — [b] Based on 1:1 stoichiometry of DBC with chloranil or DMCF. Remainder of the unreacted DBC recovered.

Table 7. Effect of tetracyanoethylene (TCNE) on the chloranil-photosensitized reactions of diphenylbenzocyclobutenes (DBC)

Donor (mmol)	Chloranil (mmol)	TCNE (mmol)	Conditions[a]	Cycloadducts %[b]
c-DBC (0.025)	(0.050)	(0.050)	Δ(50, 24) CH_2Cl_2(5 mL)	t-DTT (23)[c]
c-DBC (0.050)	(0.10)	(0.10)	Δ(3,reflux) MeCN (10 mL)	t-DTT (98)
t-DBC (0.050)	(0.10)	(0.10)	Δ(6, 24) CH_2Cl_2 (10 mL)	c-DTT (99)
c-DBC (0.025)	(0.050)	(0.050)	hν CH_2Cl_2 (5 mL)	t-DTT, c-DTT, c-DBP (19) (51) (11)
t-DBC (0.025)	(0.050)	(0.050)	hν CH_2Cl_2 (5 mL)	t-DTT, c-DTT, c-DBP (8) (58) (18)

[a] See Table 6. — [b] Based on 1:1 stoichiometry in eqs. 1/2 and 11/12. — [c] Recovered c-DBC was 77%.

and 2.8:1 with the *trans*-isomer[38]. Third, the pair of phenyl groups were extensively equilibrated in both the CA and DMCF cycloadducts. [Note however that the relative stereochemistry of the cyano and methoxycarbonyl substituents was intact.]

(B). *Tetracyanoethylene* (TCNE) showed the same effect but in a more pronounced manner owing to the diminished competition from chloranil in the thermal cycloaddition. For example, when *cis*-diphenylbenzocyclobutene was treated with an excess of a 1:1 molar mixture of TCNE and CA under thermal conditions, only TCNE adducts were formed (see entries 1–3, Table 7). In the photosensitized process, the presence of only an equimolar amount of the foreign dienophile is sufficient to trap most of the DBC as the *cis*- and *trans*-diphenyl cycloadducts of TCNE. Furthermore the *cis*-diphenyl adduct of chloranil (*c*-DBP) was the preponderant isomer formed from both *cis*- and *trans*-diphenylbenzocyclobutene.

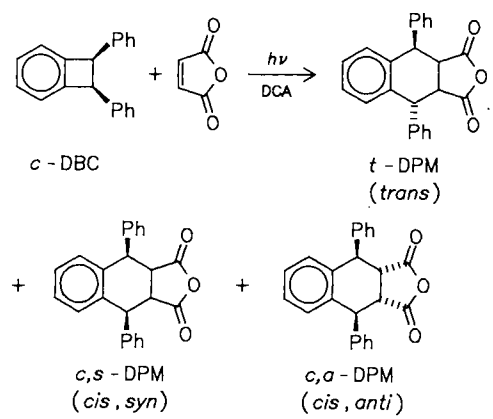
VI. DCA-Sensitized Isomerization of *cis*- and *trans*-Diphenylbenzocyclobutenes

No change was apparent when a solution of *cis*-diphenylbenzocyclobutene in either dichloromethane, acetonitrile, or benzene was treated with $5 \cdot 10^{-4}$ M 9,10-dicyanoanthracene (DCA) for prolonged times (50 h) in the dark at 24°C. However if the same solutions were irradiated with actinic light (λ > 380 nm), significant amounts of the isomeric *trans*-diphenylbenzocyclobutene were observed within an hour, as listed in Table 8. Analogously, *trans*-diphenylbenzocyclobutene was converted to the *cis*-isomer, albeit in reduced conversions.

Table 8. Dicyanoanthracene-sensitized isomerization of diphenylbenzocyclobutenes[a]

Donor (mmol)	Solvent	Additive[b] (mmol)	Product Analysis (%)[c]		
c-DBC (0.050)	CH_2Cl_2	-	c-DBC, t-DBC (59) (26)[d]		
	MeCN	-	(52) (38)[e]		
	C_6H_6	-	(90) (10)		
t-DBC (0.050)	MeCN	-	c-DBC, t-DBC (5) (94)[f]		
c-DBC (0.050)	CH_2Cl_2	(0.10)	t-DPM (75)	cs-DPM, ca-DPM (10) (tr)	
	MeCN	(0.10)	(76)	(10) (tr)[g]	
	C_6H_6	(0.10)	(13)	(tr)[h]	
t-DBC (0.050)	MeCN	(0.10)	(tr)	(78)	(20)

[a] In 2.0 ml of solvent containing $5.0 \cdot 10^{-4}$ M 9,10-dicyanoanthracene at 24°C. Actinic irradiation carried out at λ > 380 nm with Corning cutoff filter (CS-375). — [b] MA = maleic anhydride. — [c] Based on 1:1 stoichiometry 9-phenylanthracene detected in [d] ≈ 0.5%, [e] 1%, [f] 0.5% yield. *c*-DBC recovered in [g] 5% and [h] 80% yield. tr = trace (< 1%).



(17)

When the photosensitized reaction was carried out in the presence of 2 equivalents of maleic anhydride (MA), high yields of the cycloadducts DPM were formed. Interestingly, the photosensitized cycloaddition of *cis*-diphenylbenzocyclobutene to maleic anhydride was not stereospecific, since all three isomers[39,40] were found, eq. 17.

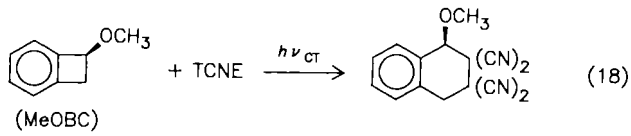
VII. Charge-Transfer Cycloaddition of Mono-Substituted Benzocyclobutenes to Tetracyanoethylene

The electron-donor properties of benzocyclobutene are strongly influenced by substituents at the 1-position, as shown by the shifts of the charge-transfer absorption bands of the EDA complexes with tetracyanoethylene in Table 9. However we could find no direct relationship between the energy of the charge-transfer transition (i.e., λ_{CT}^{-1}) and the occurrence of the CT-induced cycloaddition. For example, the actinic irradiation of the EDA complex of the parent benzocyclobutene (BC) and TCNE at $\lambda > 380$ nm for 1 hour led to no reaction, and the BC donor was recovered intact. At the other extreme, 1-acetoxybenzocyclobutene (AcOBC) which formed a TCNE complex with the highest CT-transition energy, also did not yield a cycloadduct upon exposure to actinic irradiation with $\lambda > 380$ nm for an hour. On the other hand, 1-methoxybenzocyclobutene (MeOBC) which exhibited a CT-absorption band similar to that of AcOBC with tetracyanoethylene yielded the cycloadduct in 92% yield within 1 h, eq. 18.

Table 9. Charge-transfer absorption bands of the EDA complexes of mono-substituted benzocyclobutenes with tetracyanoethylene[a]

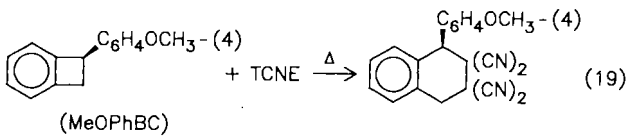
1-X-Benzocyclobutene X	CT Band (nm)[b] λ_1	λ_2
Unsubstituted	425	≈470[c]
1-Phenyl	430	≈475[c]
1-(4-$CH_3OC_6H_4$)	400	565
1-Acetoxy	390	≈450[c]
1-Methoxy	405	≈450[c]

[a] In dichloromethane solution containing $5.0 \cdot 10^{-2}$ M TCNE and $2.5 \cdot 10^{-2}$ M 1-X-benzocyclobutene. — [b] Absorption maximum, unless indicated otherwise. — [c] Shoulder.



(18)

1-Phenylbenzocyclobutene (PhBC) underwent the CT-induced cycloaddition reluctantly and the 1:1 adduct was detected in 12% yield only after irradiation for 10 hours (Table 10). The *p*-methoxyphenyl analogue (MeOPhBC) did not yield a cycloadduct even upon prolonged exposure (> 10 h) to actinic radiation with $\lambda > 380$ nm.



(19)

Table 10. CT-Induced and thermal cycloaddition of benzocyclobutenes to tetracyanoethylene

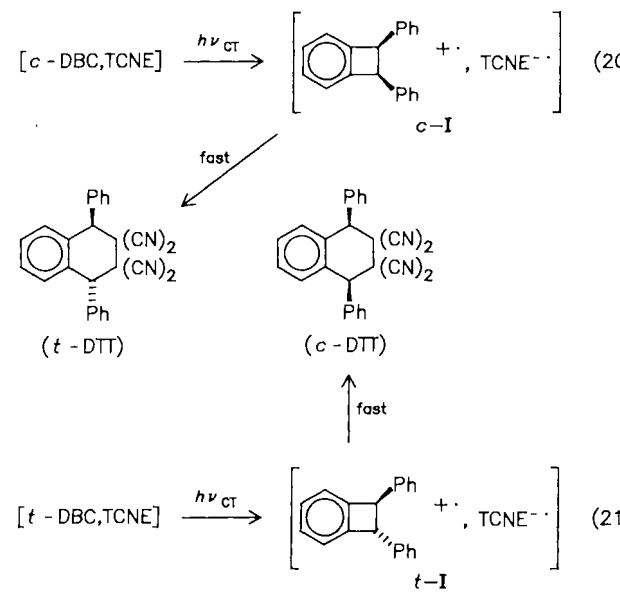
1-X-Benzocyclobutene X (mmol)	TCNE (mmol)	Conditions[a]	Products (%)[b]
Unsubstituted (0.050)	(0.050)	Δ(5, 110) $PhCH_3$ (2 ml)	BC (100)[c]
Unsubstituted (0.050)	(0.050)	hν CH_2Cl_2 (2 ml)	BC (100)[c]
Acetoxy (0.10)	(0.10)	hν CH_2Cl_2 (2 ml)	AcOBC (100)[c]
Methoxy (0.10)	(0.10)	hν CH_2Cl_2 (2 ml)	Adduct[d] (92)
Methoxy (0.10)	(0.10)	Δ(6, 110) $PhCH_3$ (2 ml)	Adduct[d] (80)[e]
p-Methoxyphenyl (0.050)	(0.050)	hν CH_2Cl_2 (2 ml)	MeOPhBC (97)[c,f]
p-Methoxyphenyl (0.10)	(0.10)	Δ(5, 110) $PhCH_3$ (2 ml)	Adduct[g] (80)
Phenyl (0.10)	(0.10)	hν CH_2Cl_2 (2 ml)	PhBC (95)[c,h]

[a] See Table 6. — [b] Based on 1:1 stoichiometry for cycloadduct. — [c] No adduct detected. — [d] 2,2,3,3-Tetracyano-1-methoxytetralin. — [e] However no reaction at 24°C for 24 h. — [f] Also reaction after irradiation for 10 h. — [g] 2,2,3,3-Tetracyano-1-(4-methoxyphenyl)tetralin. — [h] After 10 h irradiation 12% of 2,2,3,3-tetracyano-1-phenyltetralin formed and 85% of PhBC recovered.

The facility with which the benzocyclobutenes underwent the CT-induced cycloaddition also did not appear to be directly related to the ease of thermal cycloaddition. For example, MeOPhBC which was inert to tetracyanoethylene under actinic stimulation (vide supra) underwent a reasonably facile thermal cycloaddition according to eq. 19 when a toluene solution was refluxed for 5 hours.

Discussion

The bright yellow, transient color obtained immediately upon mixing the solutions of 1,2-diphenylbenzocyclobutene (DBC) and tetracyanoethylene (TCNE) indicates the for-



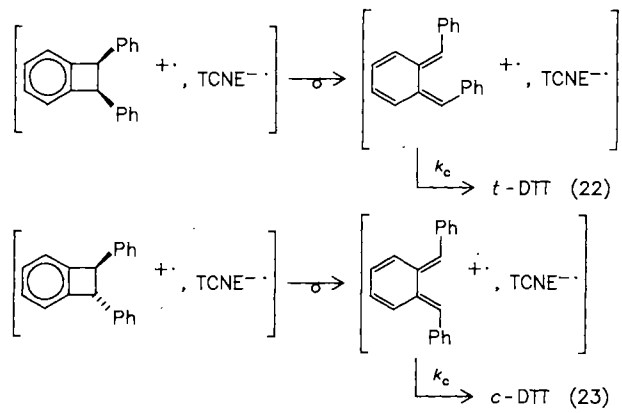
(20)

(21)

mation of an electron donor-acceptor or EDA complex. Indeed the intensity of the yellow color increases with the initial concentration of DBC and TCNE consistent with the 1:1 stoichiometry in eq. 3, as shown by the variation in the absorption band in Figure 1 according to eq. 9. Previous studies have established that the deliberate charge-transfer (CT) excitation via such an absorption band (i.e., by actinic radiation with $\lambda > 380$ nm) specifically produces the contaction pair according to eq. 4, Scheme 1[17,41]. Therefore it follows that the cycloadducts DTT formed in eqs. 10 and 11 derive from the collapse of the ion pair **I**[42], eqs. 20, 21.

The extreme rapidity with which such a collapse occurs is given by the fast cycloaddition rates (i.e., short conversion times) in Table 1 and the high quantum yields in Tables 2 and 3. Furthermore, the high stereospecificity with which the ion pairs *c*-**I** and *t*-**I** yield the cycloadducts *t*-DTT and *c*-DTT, respectively, as shown in Table 1 indicates that the cation-radical intermediates $DBC^{+\cdot}$ behave in a discrete manner, despite their transient existence. The most direct formulation for such a change involves a spontaneous ring opening to the *o*-xylylene cation radical ($XYL^{+\cdot}$), followed by the collapse of the new contact-ion pair. If so, the observed stereochemistry requires a conrotatory ring opening according to eqs. 22, 23.

Scheme 4



A preliminary laser flash photolysis of the DBC-TCNE complex presents the time-resolved spectrum between 300 and 780 nm in Figure 5. The spectral transient with the most intense band at $\lambda_{max} = 440$ nm is formed within 7.8 ns following the 25-ps laser pulse at 355 nm. Although further deconvolution of the broad absorption band is required before a definite assignment is possible, we tentatively suggest that it is an ion-pair composite of $TCNE^{-\cdot}$ ($\lambda_{max} = 425$ nm[17]) and either $DBC^{+\cdot}$ or $XYL^{+\cdot}$ (which we have as yet been unable to confirm independently by time-resolved pulse radiolysis of either *cis*- or *trans*-diphenylbenzocyclobutene). The transient absorption in Figure 5 decays with first-order kinetics ($k_1 = 3 \cdot 10^6\ s^{-1}$), consistent with ion-pair behavior.

Huisgen, Quinkert, and co-workers[14–16] have shown that the thermal cycloaddition of DBC to tetracyanoethylene occurs via diphenyl-*o*-xylylene (i.e., XYL in eqs. 1/2). Thus the

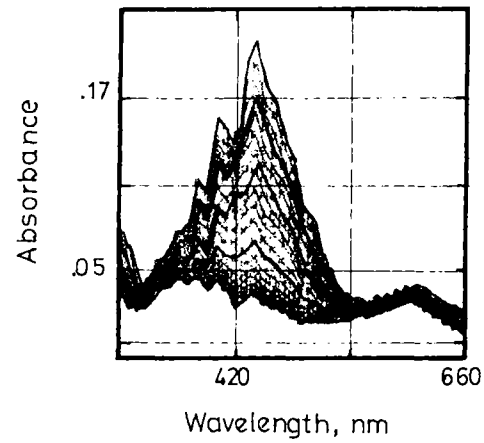
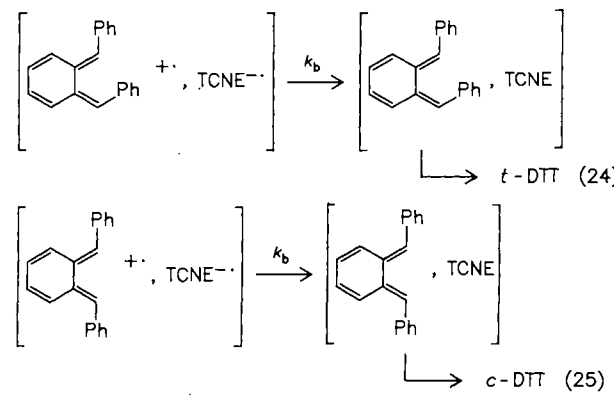


Figure 5. Spectral transient observed at 7.8 ns (top) following the 25-ps laser pulse at 355 nm of an acetonitrile solution containing $2.5 \cdot 10^{-2}$ M *cis*-1,2-diphenylcyclobutene and $5.0 \cdot 10^{-2}$ M tetracyanoethylene

comparison of eqs. 1/2 and 22/23 indicates that the cycloreversion of the benzocyclobutene moiety occurs by conrotatory ring opening in both the neutral and the cation-radical species. Indeed the correlation diagram for benzocyclobutene → *o*-xylylene is consistent with an allowed conrotatory process[43]. The same consideration for the cation-radical species poses an interesting problem since the unpaired electron occupies the π_3 SOMO in the benzocyclobutene reactant. This orbital correlates with π_2 in the *o*-xylylene indicative of an excited cation radical of the product, which is technically "forbidden". However owing to the small energy gap between π_3 and π_2, it is possible for the ground-state interconversion of $DBC^{+\cdot} \rightarrow XYL^{+\cdot}$ to occur directly with state crossing accompanying the isomerization[44]. Such a conrotatory process is energetically more favorable than the disrotatory opening which correlates π_3 with the antibonding π_5^*. Be that as it may, the CT results provide strong indication that the cycloreversion of the diphenylbenzocyclobutene cation radical is stereospecific (conrotatory), and it must occur at rates which are significantly faster than those of the neutral precursor[45]. Such an enhanced lability of the cation radical relative to its neutral precursor is a general phenomenon, and has been observed with a variety of other electron donors[46,47].

Scheme 5



As appealing as the direct pathway in Scheme 4 is for the CT-induced cycloaddition of DBC, there is at least one mechanistic alternative which merits strong consideration. Thus it is possible that the rearranged ion pairs in eqs. 22/23 undergo back electron transfer (k_b) faster than collapse (k_c)[48]. Under these conditions, the cation-radical intermediate is involved in only the ring opening (eqs. 22/23), and the cycloaddition actually involves the neutral *o*-xylylene as in the thermal process, Scheme 5[49].

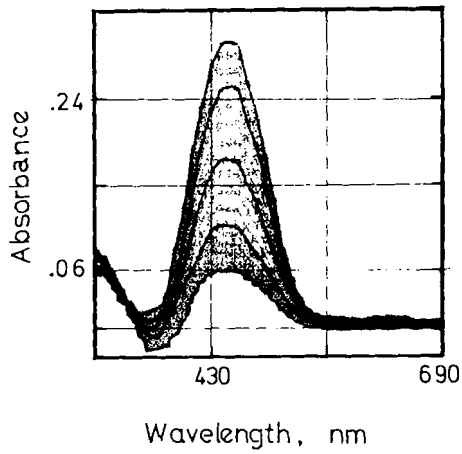
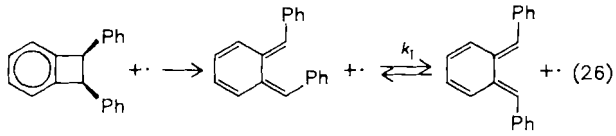


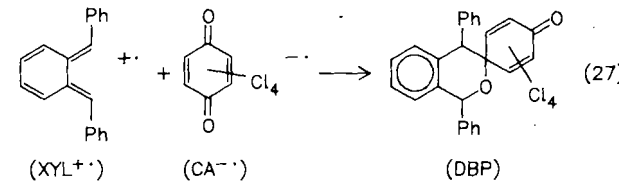
Figure 6. Time-resolved absorption spectrum of chloranil anion radical at 500 ns following the 25-ps laser pulse at 355 nm of a dichloromethane containing $2.0 \cdot 10^{-3}$ M chloranil and $2.0 \cdot 10^{-3}$ M *cis*-1,2-diphenylbenzocyclobutene

In order to evaluate the relative merits of Schemes 4 and 5, let us consider the stereochemistry of cycloaddition via the cation radical $DBC^{+\cdot}$ formed by diffusional quenching according to eqs. 5 and 6 in Scheme 2. Consistent with this formulation, we observe in Figure 6 the spectral transient tentatively assigned to $CA^{-\cdot}$ (λ_{max} = 450 nm[19]) which persists for more than 10 μs following the flash photolysis of a solution of chloranil and *cis*-1,2-diphenylbenzocyclobutene with a 25-ps laser pulse at 355 nm. The results depicted in eqs. 13/14 show that unlike the thermal process in eqs. 12a/b, the photosensitized cycloaddition of *cis*- and *trans*-DBC to chloranil is not stereospecific. Such a result is accommodated by the facile ring opening of $DBC^{+\cdot}$ followed by isomerization to $XYL^{+\cdot}$, eq. 26.

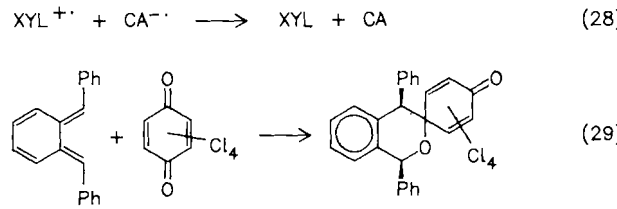


Cation radicals are formed efficiently under these photosensitized conditions (see Table 4), and they are longer-lived than those formed as intimate ion pairs **I** by charge-transfer excitation of the EDA complex as in eqs. 20/21. Indeed they are comprised of "loose" or "solvent-separated" ion pairs **II** (eq. 6), in which the cation radical $DBC^{+\cdot}$ is relatively free owing to the diffusional electron transfer from DBC to the excited triplet chloranil ^3CA which occurs over a relatively long distance of separation[50]. The longer-lived cation radical in **II** would also have a greater opportunity to undergo isomerization following ring-opening in eq. 26[51]. Thus the substantial amounts of the rearranged cycloadducts formed in the photosensitized process[52] could arise from the relatively "loose" cation radicals $XYL^{+\cdot}$ which are free to afford cycloadducts with $CA^{-\cdot}$ either directly by ion-pair annihilation, eq. 27, or indirectly by back electron transfer followed by a Diels-Alder process analogous to that represented in Scheme 5.

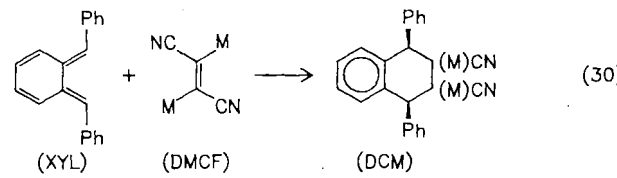
Scheme 1′



Scheme 5′



Indeed the trapping experiments described in Tables 6 and 7 establish the viability of Scheme 5′. For example, the presence of the added dienophile dimethyl dicyanofumarate (DMCF) during the chloranil-sensitized conversion of diphenylbenzocyclobutene diverts the cation radical $DBC^{+\cdot}$ to the new cycloadduct DCM in entries 4 and 5, Table 6. Such a diversion of the loose ion pair $[XYL^{+\cdot},CA^{-\cdot}]$ is most likely to occur by back electron transfer (eq. 28) followed by a competition for the neutral XYL by either chloranil as in eq. 29 or by the added dienophile, eq. 30.



Indeed the stereochemistry observed in the DCM adducts coincides with those derived from XYL in the thermal process in eqs. 15/16. Furthermore the extensive equilibration of the phenyl substituents in the cycloadducts from both chloranil and dimethyl dicyanofumarate is consistent with the long-lived cation radical in eqs. 26.

If Scheme 5′ were the only pathway by which the photosensitized cycloaddition occurred, the competition between CA and DMCF for the *o*-xylylene intermediate would be dictated by the relative rates of eqs. 29 and 30. This ratio is established in the competition experiments between eqs. 12a and 15, as listed by entries 1 and 2 in Table 6. The fact

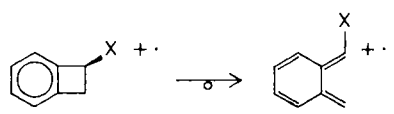
that the photosensitized process leads to a higher fraction of chloranil adducts than that obtained thermally suggests the presence of an alternative pathway involving ion-pair annihilation presented in eq. 27 (Scheme 1′). The alternative pathway for the interception by DMCF is less likely since it requires the electron transfer between the acceptors to be facile[53], eqs. 31, 32.

$$CA^{-\cdot} + DMCF \longrightarrow CA + DMCF^{-\cdot} \quad (31)$$

$$DMCF^{-\cdot} + XYL^{+\cdot} \longrightarrow DCM \quad (32)$$

Evidence of the viability of Scheme 1′ is also obtained from the use of tetracyanoethylene as the dienophilic trap. Since TCNE is a much better dienophile than chloranil, the thermal competition between eqs. 1 and 29 heavily favors the DTT cycloadduct, as shown in entries 1–3 in Table 7. Thus the significant amounts of the chloranil adduct DBP in the CA-photosensitized activation of diphenylbenzocyclobutene in entries 4 and 5 (Table 7) support an important contribution of Scheme 1′ to the overall cycloaddition process. It is also noteworthy that extensive equilibration of the phenyl substituents is observed in *both* the chloranil and tetracyanoethylene adducts., in accord with the isomerization in eq. 26. Indeed *cis*- and *trans*-diphenylbenzocyclobutene both undergo extensive isomerization in the act of quenching the excited singlet of 9,10-dicyanoanthracene in entries 2–4 (Table 8). Under these conditions, the $DBC^{+\cdot}$ formed as the loose ion pair **III** in eqs. 8 (Scheme 3) has no recourse to cycloaddition. As a result, the equilibration of the phenyl substituents is optimized by the isomerizations in eq. 26, followed by back electron transfer to regenerate the rearranged diphenylcyclobutene. The trapping by maleic anhydride in entries 5–8 (Table 8) is analogous to that observed during chloranil photosensitization in Tables 6 and 7.

Finally we wish to emphasize that cycloreversion by electron transfer is not restricted to diphenylbenzocyclobutene. It also occurs readily in the mono-substituted benzocyclobutene with a methoxy substituent and to a limited extent with 1-phenylbenzocyclobutene (see Table 10). On the other hand, we have been unable to observe electron-transfer activation of the parent benzocyclobutene and the 1-acetoxy and 1-(4-methoxyphenyl) derivatives despite similarities in the donor properties as shown by the comparison of the charge-transfer spectra in Table 9. The difference may be ascribable to the substituent effect on the ease of the cycloreversion as in eq. 33 relative to back electron transfer. However the detailed interplay of steric, inductive, and resonance contributions are not so clear since the trend in Table 10 more or less follows the order: X = MeO ≫ Ph > H ≈ AcO ≈ MeOPh[54,55]. It is particularly noteworthy that this differs from the thermal cycloadditions in which the analogues with X = MeO and MeOPh are *both* reactive.



(33)

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Experimental

Materials: Tetracyanoethylene (Aldrich) was purified by successive sublimations until colorless. Chloranil (Aldrich) was recrystallized repeatedly from acetone and dried in vacuo. Dimethyl dicyanofumarate was prepared from methyl cyanoacetate (Aldrich) and thionyl chloride[56a]. Maleic anhydride from Aldrich was purified by vacuum sublimation prior to use. 9,10-Dicyanoanthracene was synthesized according to the literature method[56b] and recrystallized from benzene/ethanol. *cis*- and *trans*-1,2-diphenylbenzocyclobutene were prepared by a sequence of seven steps from phthalic anhydride, as described by Carpino[57]. The *trans*-isomer was obtained by this procedure as a slightly yellow solid in 91% yield. Recrystallization from dichlormethane/ethanol yielded 77% of colorless crystals, m.p. 93–94°C. The ^{1}H-NMR spectrum (90 MHz) in $CDCl_3$ showed the characteristic singlet resonance for the methine protons at δ 4.47 (2H) as well as the aromatic protons as an unresolved multiplet centered at δ 7.30 (14H). *cis*-1,2-Diphenylbenzocyclobutene was obtained by a similar procedure[57] as a wide-melting yellow solid (70%), which was contaminated with ≈ 20% of the *trans*-isomer. It was purified by column chromatography on silica gel with *n*-hexane as eluent, followed by repeated crystallization from dichloromethane/ethanol to finally yield colorless crystals in 21% yield, m.p. 83–84°C (ref.[57] 85.5–87.5°C. – ^{1}H-NMR ($CDCl_3$): δ 5.19 (s, 2H), 6.90 (m, 2H), 7.35 (m, 4H).

Instrumentation: Electronic spectra (300–650 nm): Hewlett-Packard 8450A diode-array spectrometer. – ^{1}H-NMR spectra: Jeol FX-90Q (90 MHz) or Nicolet NT 300 (300 MHz) spectrometers. – IR spectra: Nicolet 10-DX fourier transform spectrometer. – X-ray crystallography: Enraf-Nonius CAD-4 automatic diffractometer, Mo-K_α radiation. – Actinic radiation was produced by a high pressure 1-kW mercury-xenon lamp (Hanovia 977B0010) provided with an aqueous IR heat filter and either a Corning cutoff or an interference filter, as specified below. – The time-resolved absorption spectra on the ns timescale were obtained with the 25-ps laser flash system described previously[42].

Diels-Alder Adducts from the Thermal Reaction of cis- and trans-1,2-Diphenylbenzocyclobutene with Tetracyanoethylene

The solution of *cis-1,2-diphenylbenzocyclobutene* (12.8 mg, 0.050 mmol) and 12.8 mg (0.10 mmol) of tetracyanoethylene (TCNE) in 2 ml of acetonitrile was stirred at 75°C for 3 h. The reaction mixture was concentrated in vacuo, and the resultant solid chromatographed on a silica-gel column with *n*-hexane/dichloromethane (1:1) as eluent. The various fractions containing the adduct were collected. Removal of the solvent in vacuo afforded 18 mg (0.094 mmol, 94%) of a colorless solid; m.p. 221–223°C. Recrystallization from dichloromethane/ether afforded 13 mg of colorless plates of *trans*-2,2,3,3-tetracyano-1,4-diphenyltetralin, m.p. 223–224°C° (ref.[15] 225.5–227.0°C). – ^{1}H NMR ($CDCl_3$): δ 5.19 (s, 2H), 6.98 (m, 2H), 7.29 (m, 2H), 7.52 (br s, 10H). – IR (KBr): 3062 cm^{-1}, 3035, 3012, 2898, 2258 (ref.[15] 2222), 1491, 1456, 784, 756, 731, 713, 703. – None of the *cis*-isomer (< 2%, vide infra) could be detected.

The same reaction of *cis*-DBC with TCNE carried out at 25°C afforded only 7% of *t*-DTT after 24 h and > 90% of recovered starting materials.

The solution of *trans-1,2-diphenylbenzocyclobutene* (12.8 mg, 0.050 mmol) and 7.0 mg (0.055 mmol) of TCNE in 2 ml of dry dichloromethane was stirred at room temperature. The yellow-red solution was gradually bleached over a period of 6 h. The solvent was removed in vacuo, and the resultant solid was chromatographed over silica gel. Elution with *n*-hexane/dichloromethane (1:1) yielded 19 mg (0.049, mmol, 99%) of the colorless TCNE adduct wich melted at 227–228°C. Recrystallization from dichloromethane/ether gave 16 mg (84%) of fine colorless needles of *cis*-2,2,3,3-tetracyano-1,4-diphenyltetralin, m.p. 227–228°C (ref.[15] 229–231°C). – ^{1}H NMR ($CDCl_3$): δ 5.11 (m, 2H), 7.35 (m, 2H), 7.48 (s, 10H). – IR (KBr): 3066 cm^{-1}, 3035, 2906, 2890, 2254, (ref.[15] 2237), 1494, 1456, 1447, 750, 741, 706. – None of the *trans*-isomer (< 2%, vide supra) could be detected.

Diels-Alder Adducts of cis- and trans-1,2-Diphenylbenzocyclobutene with Dimethyl Dicyanofumarate

trans-1,2-Diphenylbenzocyclobutene (12.8 mg, 0.050 mmol) and 9.8 mg (0.051 mmol) of dimethyl dicyanofumarate were dissolved in 2 ml of dry dichloromethane. After stirring the solution for 6 h at room temperature the solvent was removed in vacuo. Chromatography of the residue (23 mg) on silica gel with benzene/*n*-hexane (1:1) as the eluent afforded 22 mg (0.049 mmol, 97%) of a colorless solid (R_f = 0.40) as the sole product. Recrystallization from dichloromethane/hexane afforded 21 mg of the colorless needles of *trans*-2,3-dicyano-*trans*-2,3-bis(methoxycarbonyl)-*cis*-1,4-diphenyltetralin, m.p. 188–189°C. – ^{1}H NMR ($CDCl_3$): δ 3.50 (s, 3H), 3.81 (s, 3H), 5.04 (s, 1H), 5.36 (s, 1H), 7.0–7.4 (w, 14H). – IR (KBr): 3065 cm^{-1}, 3037, 2959, 2250, 1763, 1738.

$C_{28}H_{22}N_2O_4$ (450.5) Calcd. C 74.65 H 4.92 N 6.22
Found[58] C 74.66 H 4.97 N 6.21

cis-1,2-Diphenylbenzocyclobutene (26.5 mg, 0.10 mmol) and 39 mg (0.20 mmol) of dimethyl dicyanofumarate were dissolved in 4 ml of dry acetonitrile. After stirring at 75°C for 3 h the solvent was removed in vacuo. ^{1}H-NMR analysis of the residual dissolved in $CDCl_3$ indicated the presence of two different methoxy resonances at δ 3.54 and 3.60 in a ratio of 3:7 as well as two distinct methine resonances at δ 5.51 and 5.40 in the ratio of 3:7. The mixture upon TLC over silica gel with benzene showed two resolved bands with R_f = 0.70 and 0.50. The minor upper band afforded 10 mg (0.022 mmol, 22%) of one Diels-Alder adduct, and the major lower band yielded 30 mg (0.067 mmol, 67%) of another Diels-Alder adduct. None of the *cis*-1,4-diphenyl isomer (vide supra) was produced. Recrystallization of the minor adduct from dichloromethane/hexane yielded 6 mg (13%) of colorless prisms, m.p. 249–250°C. – ^{1}H NMR ($CDCl_3$): δ 3.54 (s, 6H), 5.51 (s, 2H), 6.93 (m, 2H), 7.14 (m, 2H), 7.38 (m, 10H). – IR (KBr): 3066 cm^{-1}, 3031, 2951, 2250, 1749, 1744, 1259, 1228, 750, 706.

$C_{28}H_{22}N_2O_4$ (450.5) Calcd. C 74.65 H 4.92 N 6.22
Found[58] C 74.58 H 4.96 N 6.19

Recrystallization of the major isomer from hexane/dichloromethane yielded 22 mg (0.049 mmol, 49%) of colorless crystals, m.p. 246–247°C. – ^{1}H NMR ($CDCl_3$): δ 3.60 (s, 6H), 5.40 (s, 2H), 6.92 (m, 2H), 7.18 (m, 2H), 7.40 (m, 10H). – IR (KBr): 3031 cm^{-1}, 3008, 2953, 2258, 1766, 1750, 1262, 1234, 722, 703.

$C_{28}H_{22}N_2O_4$ (450.5) Calcd. C 74.65 H 4.92 N 6.22
Found[58] C 74.60 H 4.95 N 6.23

Thermal Cycloaddition of cis-1,2-Diphenylbenzocyclobutene to Chloranil (CA): The thermal interaction of *cis*-1,2-diphenylbenzocyclobutene and chloranil was carefully examined under three conditions.

Method A: cis-1,2-Diphenylbenzocyclobutene (12.8 mg, 0.050 mmol) and 24.6 mg (0.10 mmol) of chloranil were dissolved in 5 ml of acetonitrile. After heating the mixture at 75°C for 3 h the solvent was removed in vacuo. The ^{1}H-NMR spectrum of the yellow residue dissolved in $CDCl_3$ was consistent with the presence of only one product which was confirmed by a single spot on TLC (silica gel). Elution with benzene afforded 23 mg (0.046 mmol, 91%) of a pale yellow solid (R_f = 0.60). Crystallization from dichloromethane/isopropyl alcohol yielded 19 mg (76%) of colorless prisms of the *trans*-cycloadduct (vide infra), m.p. 181–182°C.

Method B: cis-1,2-Diphenylbenzocyclobutene (12.8 mg, 0.050 mmol) and 24.6 mg (0.10 mmol) of chloranil were dissolved in 10 ml of dry dichloromethane. After the solution was stored in the dark for 96 h the solvent was removed in vacuo. ^{1}H-NMR analysis of the yellow solid using 4-nitrotoluene as the internal standard (δ 2.46) indicated the presence of 0.011 mmol (22%) of the *trans*-cycloadduct (vide infra) together with 0.038 (75%) of unreacted *cis*-diphenylbenzocyclobutene.

Method C: cis-1,2-Diphenylbenzocyclobutene (5.2 mg, 0.020 mmol) and 5.0 mg (0.020 mmol) of chloranil were dissolved in 1 ml of CD_2Cl_2. The solution was allowed to stand at room temp. in the dark, and the ^{1}H-NMR spectrum was examined periodically over a period of a month. The gradual disappearance of the methine proton of *cis*-diphenylbenzocyclobutene at δ 5.22 was accompanied by the concomitant growth of a pair of new singlets at δ 5.02 and 6.58. None of the resonances due to the adduct(s) derived from the isomeric *trans*-diphenylbenzocyclobutene (vide infra) were detected. Removal of the solvent in vacuo afforded 10 mg (0.020 mmol, 100%) of a pale yellow solid. Crystallization from dichloromethane/isopropyl alcohol gave 7 mg (70%) of colorless prisms, m.p. 181–182°C. – ^{1}H NMR ($CDCl_3$): δ 4.98 (s, 1H), 6.57 (s, 1H), 7.0 – 7.45 (m, 14H). – IR (KBr): 3063 cm^{-1}, 3031, 2401, 2390, 1688, 1575, 1494, 1456, 1275, 1109, 1019, 969, 925, 906, 816, 750, 728, 700. – UV-VIS (λ_{max}, ε_{max}, in MeCN): 255 nm (9740), 300 (sh, 3840).

Thermal Cycloaddition of trans-1,2-Diphenylbenzocyclobutene to Chloranil

trans-1,2-Diphenylbenzocyclobutene (12.8 mg, 0.050 mmol) and 12.3 mg (0.050 mmol) of chloranil were dissolved in 5 ml of dichloromethane. After the solution was stirred at room temp. for 6 h the solvent was removed in vacuo. The ^{1}H-NMR spectrum (90 Hz) of the yellow solid (25 mg) dissolved in $CDCl_3$ at 23°C showed two singlets at δ 5.03 and 6.26 and a multiplet at δ 6.62 in addition to aromatic resonances (7.1–7.6 ppm) in the ratio of 1:1:1: ≈ 15. Essentially the same ^{1}H-NMR spectrum was obtained in [D_3]acetonitrile and [D_6]acetone. Crystallization of the yellow solid from dichloromethane/isopropyl alcohol yielded 20 mg (0.040 mmol, 80%) of colorless prisms, m.p. 161–170°C (coloration at ≈ 168°C). ^{1}H-NMR analysis showed the presence of the same resonances found above. Repeated attempts to resolve the material by various chromatographic methods were unfruitful. – IR (KBr): 3066 cm^{-1}, 3031, 3008, 2401, 2390, 1681, 1606, 1575, 1490, 1456, 1275, 1109, 1006, 969, 925, 906, 816, 747, 728, 700. – UV-VIS (λ_{max}, ε_{max} in MeCN): 253 nm (8740), 291 (6220).

$C_{26}H_{16}Cl_4O_4$ (502.2) Calcd. C 62.18 H 3.21 Cl 28.24
Found C 62.25 H 3.23 Cl 28.28

The IR and UV-VIS spectra and the elemental analyses are consistent with a 1:1 adduct of *trans*-diphenylbenzocyclobutene and chloranil which is similar to the structure of the *cis*-cycloadduct (vide supra). Thus the pair of singlets at δ 5.03 and 6.26 in the ^{1}H-NMR spectrum is reasonable for an isomeric 1:1 *cis*-adduct since

trans-cycloadduct (vide supra) shows a similar pair of singlet resonances at δ 4.98 and 6.57. However the unidentified multiplet at δ 6.62 raises some question as to whether another isomeric adduct distinct from those above (but not separable by crystallization) may not be formed. Alternatively, the multiplet may be due to one of the aromatic hydrogens which has been shifted upfield (perhaps by an anisotropic ring current absent in the conformationally more rigid *trans*-isomer). The ^{1}H-NMR spectrum at higher field (300 MHz) and 17°C showed a 1:1 doublet splitting at δ 6.63 (J = 7.3 Hz) in addition to the other resonances.

Charge-Transfer Photochemistry of the EDA Complex of cis- and trans-Diphenylbenzocyclobutene and Tetracyanoethylene

cis-1,2-Diphenylcyclobenzocyclobutene: The CT excitation of the EDA complex of *cis*-1,2-diphenylbenzocyclobutene and tetracyanoethylene was carried out under argon in a 10-mm cuvette containing $2.5 \cdot 10^{-2}$ M donor and $5.0 \cdot 10^{-2}$ M TCNE in 2 ml of solvent (usually dichloromethane). The actinic radiation from a 1-kW Hg-Xe lamp was passed first through an aqueous IR heat filter and then a sharp cutoff filter (Corning CS 3–75) which eliminated radiation below 380 nm. After the photolysis (see Table 1) the reaction mixture was concentrated in vacuo. The resulting residue was chromatographed on silica gel with *n*-hexane to elute the unreacted diphenylbenzocyclobutene and then hexane/dichloromethane (2:1) to elute the Diels-Alder adduct. Each fraction was concentrated in vacuo and quantitatively analyzed by ^{1}H-NMR spectroscopy using toluene as the internal standard. The fraction containing the Diels-Alder adduct (Table 1) was analyzed further by HPLC. Spectral comparison with the Diels-Alder adduct obtained from the thermal reaction of *cis*-1,2-diphenylbenzocyclobutene and tetracyanoethylene (vid supra) proved it to be identical. None of the isomer (< 2%) from the *trans*-isomer could be detected (see Table 1).

trans-1,2-Diphenylbenzocyclobutene: The CT excitation of the EDA complex of $2.5 \cdot 10^{-2}$ M *trans*-1,2-diphenylbenzocyclobutene and $5.0 \cdot 10^{-2}$ M TCNE was carried out in 2 ml of dichloromethane by the procedure described above. The ^{1}H-NMR spectrum of the Diels-Alder adduct obtained by silica-gel chromatography was identical with that obtained from the thermal reaction of *trans*-1,2-diphenylbenzocyclobutene and TCNE (vide supra). None of the isomer from the *cis*-isomer (< 2%) could be detected. (Table 1). In order to establish that the thermal cycloaddition of TCNE to *trans*-diphenylbenzocyclobutene did not offer significant competition to the CT process, *t*-DBC (0.050 mmol, 12.8 mg) in 1.6 ml of dichloromethane was placed in a 10-mm cuvette which was cooled to −46°C. To this solution 0.40 ml of a MeCN solution containing 0.050 mmol of TCNE was added and the contents mixed rapidly. The change in the CT absorbance at 0, 10, 20, 30, 40, and 60 min was 0.385, 0.383, 0.386, 0.378, and 0.366, respectively. By comparison, the absorbance of a similar solution irradiated at λ > 380 nm decreased from 0.388 to 0.353, 0.334 and 0.309 from 0, 5, 10, and 15 min at the same temperature. We conclude from these data the CT process is > 20 times faster than the thermal process at −46°C. The factor is > 100 for *c*-DBC owing to an imperceptible thermal process for cycloaddition.

Quantum Yield for the CT-Induced Cycloaddition of Diphenylbenzocyclobutene to Tetracyanoethylene: The quantum yield for the charge-transfer-induced cycloaddition of diphenylbenzocyclobutenes to TCNE was carried out with the *cis*-isomer owing to its diminished rate of thermal reaction (vide supra). Typically, a solution of *cis*-1,2-diphenylbenzocyclobutene (0.050 mmol) and TCNE (0.10 mmol) in 2 ml of dichloromethane was irradiated with light from 1-kW mercury-xenon lamp after it was passed through an aqueous IR heat filter and then through various interference filters (see Table 2) all with 10-nm band widths (fwhm). The course of the CT photochemical reaction was followed by measuring the decrease in the absorbance of the CT band. The light intensity at the various wavelengths (see Table 2) was determined by Reinecke salt actinometry[33,34].

Photosensitized Cycloaddition of cis- and trans-Diphenylbenzocyclobutene to Chloranil

cis-1,2-Diphenylbenzocyclobutene (0.050 mmol) and chloranil (0.10 mmol) were dissolved in 10 ml of dichloromethane, and the solution was deaerated with a stream of argon. The pyrex tube was exposed to radiation from a 1-kW mercury-xenon lamp which was first passed through an aqueous IR heat filter and then through a cutoff filter (Corning CS 3–75) to remove light with λ < 380 nm. After a short irradiation at 24°C for 3 min the solvent was removed in vacuo and replaced with $CDCl_3$ containing 4-nitrotoluene as the internal standard for ^{1}H-NMR analysis.

trans-1,2-Diphenylbenzocyclobutene (0.050 mmol) and chloranil (0.10 mmol) were dissolved in 10 ml of dichloromethane. The solution was irradiated at 24°C with the filtered light (for λ < 380 nm, as described above) for 3 min. The composition of the cycloadducts is presented in eq. 14.

Quantum Yield for the Photosensitized Cycloaddition of cis-Diphenylbenzocylobutene to Chloranil: Owing to the rather slow thermal reaction of *cis*-1,2-diphenylbenzocyclobutene with chloranil, the quantum yield of the photosensitized process could be examined directly by following the temporal decrease in the absorbance of chloranil (λ_{max} = 377 nm, ε_{max} = 820 mol^{-1} cm^{-1}). Typically, a 2-ml solution of $1.0 \cdot 10^{-2}$ M chloranil and $5.0 \cdot 10^{-3}$ M *cis*-1,2-diphenylbenzocyclobutene in dichloromethane was irradiated at 405 nm with light passed through an interference filter (Ditric) with 10-nm band pass (fwhm). The photoreaction was carried out to only ≈ 5% conversion, and the light intensity was measured by Reinecke salt actinometry[34]. The dependence of the quantum yield on the concentration of the diphenylbenzocyclobutene is given in Table 4.

Effects of Added Dienophiles on the Photosensitized Cycloaddition of Diphenylbenzocyclobutene to Chloranil: In a typical procedure, a mixture of chloranil (0.50 mmol) and dimethyl dicyanofumarate (0.25 mmol) or tetracyanoethylene (0.050 mmol) was dissolved in 5 ml of dichloromethane. To this was added either *cis*- or *trans*-1,2-diphenylbenzocyclobutene (0.025 mmol), and the contents in the pyrex tube were deaerated with a stream of argon. The solution was irradiated for ≈ 3 min with filtered light from a 1-kW mercury-xenon lamp equipped with a sharp Corning cutoff filter to remove radiation < 380 nm. The solvent was removed in vacuo and replaced with $CDCl_3$. ^{1}H-NMR analysis (Table 6) was carried out with 4-nitrotoluene as the internal standard.

Charge-Transfer Spectra of Diphenylbenzocyclobutene with Dienophiles. Formation Constants of the EDA Complexes: The spectral changes accompanying the exposure of *cis*- and *trans*-1,2-diphenylbenzocyclobutene to various dienophiles were measured immediately after mixing the dichloromethane solutions of each colorless component. The CT spectra from tetracyanoethylene in Figure 1 are characteristic of intermolecular electron donor-acceptor complexes of this dienophile with arenes[41]. The formation constants were determined by the Benesi-Hildebrand method[24,25] using the aromatic donor in at least tenfold excess. The change in the CT absorbance of the *trans*-isomer (Table 11) was measured at λ_{max} = 404 nm. Owing to a slight complication from a slow thermal reaction, the initial absorbance was obtained by extrapolation of the absorbances taken at 15 s intervals.

Dimethyl dicyanofumarate forms weaker EDA complexes with the diphenylbenzocyclobutenes in dichloromethane. For example,

Table 11. Formation constants of the EDA complexes of 1,2-diphenylbenzocyclobutenes and tetracyanoethylene[a]

DBC (10^2 M)	A[b] (M^{-1} cm $^{-1}$)	[TCNE]/A
cis 2.00	0.0384	0.0521
cis 2.34	0.0453	0.0442
cis 2.85	0.0546	0.0366
cis 3.63	0.0692	0.0289
cis 5.00	0.0933	0.0214
trans 1.99	0.0242	0.0827
trans 2.33	0.0276	0.0725
trans 2.85	0.0336	0.0596
trans 3.62	0.0415	0.0483
trans 5.01	0.0595	0.0337

[a] In 2 ml of dichloromethane containing $2 \cdot 10^{-3}$ M tetracyanoethylene at 24°C. — [b] Measured at 416 and 404 nm for *cis*- and *trans*-DBC, respectively.

when 0.10 mmol of DMCF was added to 2 ml of dichloromethane containing 0.050 mmol of *cis*-DBC, the low energy tail of the DMCF absorption (cutoff at 360 nm) was red-shifted slightly so that the absorbance at 380 nm increased from 0 to 0.17 and that at 400 nm to 0.12. No CT maximum was observed (compare the CT absorption with TCNE in Figure 1). Actinic irradiation of this solution with $\lambda > 380$ nm for 1 h led to *t,a,t*-DCM and *t,s,t*-DCM in 34 and 12% yields, respectively (compare the thermal reaction in eq. 15). *c*-DBC was recovered in 51% yield.

The EDA complexes of chloranil with the diphenylbenzocyclobutenes were too weak to measure under the conditions comparable to those described above for TCNE. Thus the absorption spectrum of a dichloromethane solution containing $1.0 \cdot 10^{-2}$ M chloranil and $5.0 \cdot 10^{-3}$ M *cis*-diphenylbenzocyclobutene was essentially the same as that containing only the aromatic donor. The CT results in Table 5 were obtained at significantly higher concentrations of the aromatic donors.

DCA-Sensitized Isomerization of the Diphenylbenzocyclobutenes. Trapping by Maleic Anhydride: A solution containing $5.0 \cdot 10^{-4}$ M 9,10-dicyanoanthracene and $5.0 \cdot 10^{-2}$ mmol of either *cis*- or *trans*-1,2-diphenylbenzocyclobutene in 2 ml of the appropriate solvent was irradiated for 1 h at $\lambda > 380$ nm as described above. Thereupon the solvent was removed in vacuo and replaced by $CDCl_3$ for ^{1}H-NMR analysis.

Comparable solutions containing 0.10 mmol of maleic anhydride were treated in a similar manner. The *trans*-adduct (*t*-DPM) obtained as the sole product from *c*-DBC showed characteristic resonances at δ 3.81(m) and 4.69(m) for the α and β protons, respectively, in the ^{1}H-NMR spectrum. The isomeric *t*-DBC yielded two cycloadducts with maleic anhydride, the *cis,syn*-adduct (cs-DPM) showing resonances at δ 3.93 (dd, J = 4.0; 1.5 Hz, 2H) and 4.40 (dd, J = 4.0; 1.5 Hz, 2H) whereas the *cis,anti*-isomer showed resonances at δ 3.78 (m, 2H) and 4.28 (m, 2H) for the α and β protons, respectively.

CT-Induced Cycloaddition of Mono-Substituted Benzocyclobutenes to Tetracyanoethylene: In a general procedure, the appropriate benzocyclobutene (0.050 mmol) and tetracyanoethylene (0.10) were dissolved in 2 ml dichloromethane, and the solution was deaerated with a stream of argon. The actinic irradiation was carried out with a 1-kW Hg-Xe lamp equipped with an aqueous IR filter and a Corning CS-375 sharp cutoff filter which removed light with $\lambda <$ 380 nm. The cycloadducts were isolated by column chromatography and determined by the following physical data. 2,2,3,3-Tetracyano-1-methoxytetralin: m. p. 142–143°C. — ^{1}H-NMR ($CDCl_3$): δ = 3.71 (1H, d, J = 17.5 Hz); 3.95 (1H, d, J = 17.5 Hz); 4.00 (3H, s); 5.10 (1H, s); 7.22 (1H, m); 7.49 (3H, m).

$C_{15}H_{10}N_4O$ (262.2) Calcd. C 68.69 H 3.84 N 21.36
Found[58] C 68.77 H 3.87 N 21.34

2,2,3,3-Tetracyano-1-phenyltetralin: m. p. 147.5–148.5°C. — ^{1}H-NMR ($CDCl_3$): = 3.80 (1H, d, J = 17.3 Hz); 4.12 (1H, d, J = 17.3 Hz); 4.95 (1H, s); 6.93 (1H, m); 7.2–7.6 (8H, m).

$C_{20}H_{12}N_4$ (308.3) Calcd. C 77.90 H 3.92 N 18.17
Found[58] C 77.89 H 3.96 N 18.12

Table 12. Data collection and processing parameters for the cycloadducts of *c*-1,2-diphenylbenzocyclobutene to chloranil and dimethyl dicyanofumarate

		t-DBP	*t,a,t*-DCM (major)
Space group		$P\bar{1}$, triclinic	$P2_1/n$, monoclinic
Cell constants	a	8.979(2)Å	10.364(3) Å
	b	11.739(4)	20.533(7)
	c	12.344(6)	11.151(3)
	α	111.97(3)°	
	β	106.86(3)	101.28(4)°
	γ	97.56(3)	
	V	1112 Å^3	2327 Å^3
Molecular formula		$C_{26}H_{16}Cl_4O_2$	$C_{28}H_{22}N_2O_4$
Formula weight		502.2	450.5
Formula units per cell	Z	2	4
Density	ϱ	1.50 g cm^{-3}	1.29 g cm^{-3}
Absorption coefficient	μ	5.56 cm^{-1}	0.81 cm^{-1}
Radiation (Mo-K_α)	λ	0.71073 Å	0.71073 Å
Collection range		$4° < 2\Theta < 46°$	$4° < 2\Theta < 45°$
Scan width	$\Delta\Theta$	$(1.10 + 0.35 \tan\Theta)°$	$(0.90 + 0.35 \tan\Theta)°$
Maximum scan time		120 s	90 s
Scan speed range		0.4 to 5.0° min^{-1}	0.7 to 5.0° min^{-1}
Total data collected		3076	3137
Independent data, $I > 3\sigma(I)$		1456	1840
Total variables		289	307
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$		0.059	0.042
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$		0.058	0.041
Weight	w	$\sigma(F)^{-2}$	$\sigma(F)^{-2}$

The thermal cycloadditions were carried out at similar concentrations in refluxing toluene solution (≈ 110°C) for various lengths of time as indicated in Table 10. The thermal cycloadducts from 1-methoxy- and 1-phenylbenzocyclobutene showed their spectral properties to be identical with those of photo-cycloadducts.

The adduct from 1-(4-methoxyphenyl)benzocyclobutene was identified by the following physical properties: m. p. 163 – 164°C. – ^{1}H-NMR ($CDCl_3$): δ = 3.79 (1H, d, J = 17.0 Hz); 3.87 (3H, s); 4.10 (1H, d, J = 17.0 Hz); 6.98 (1H, m); 7.00 (2H, d, J = 9.0 Hz); 7.31 (5H, m).

$C_{21}H_{14}N_4O$ (338.3) Calcd. C 74.54 H 4.17 N 16.56
Found[58] C 74.46 H 4.19 N 16.53

X-Ray Crystallography of the Cycloadducts of cis-1,2-Diphenylbenzocyclobutene to Chloranil and Dimethyl Dicyanofumarate[59].

t-DBP (CA/*c*-DBC adduct): A small clear colorless prismatic plate of dimensions 0.40 × 0.25 × 0.13 mm was mounted on a glass fiber in a random orientation on an Enraf-Nonius CAD-4 automatic diffractometer. The radiation used was Mo-K_α monochromatized by a dense graphite crystal assumed for all purposes to be 50% imperfect. Final cell constants as well as other information pertinent to data collection and refinement are listed in Table 12.

The Laue symmetry was determined to be , and the space group was shown to be either $P1$ or 1. Intensities were measured with the Θ – 2Θ scan technique with the scan rate depending on the net

Table 13. Final atomic coordinates for non-hydrogen atoms of the cycloadducts from *cis*-DBC[a]

t-DBP (chloranil adduct)

Atom	x	y	z	B(Å^2)	Atom	x	y	z	B(Å^2)
C11	0.1116(3)	0.9002(3)	0.3846(2)	5.63(8)	C11	0.138(1)	0.8528(9)	-0.0908(8)	6.0(3)
C12	0.2187(3)	1.1411(2)	0.3421(3)	6.21(9)	C12	0.028(1)	0.8350(9)	-0.0397(9)	6.1(3)
C13	0.7350(3)	0.9922(3)	0.2678(2)	5.99(8)	C13	0.061(1)	0.7851(8)	0.0463(8)	4.5(3)
C14	0.6403(3)	0.7580(2)	0.3181(2)	4.90(8)	C14	0.281(1)	0.5794(8)	0.1584(8)	3.6(3)
O1	0.4899(8)	1.1336(5)	0.2616(5)	5.8(2)	C15	0.293(1)	0.4996(8)	0.0475(8)	4.7(3)
O2	0.3723(7)	0.7730(5)	0.4118(5)	3.7(2)	C16	0.339(1)	0.3900(9)	0.0377(9)	5.7(4)
C1	0.274(1)	0.9224(8)	0.3425(7)	3.1(3)	C17	0.381(1)	0.3608(9)	0.140(1)	6.5(4)
C2	0.320(1)	1.0276(8)	0.3291(7)	3.5(3)	C18	0.371(1)	0.4385(9)	0.2500(8)	5.4(3)
C3	0.460(1)	1.0467(8)	0.2886(7)	3.9(3)	C19	0.326(1)	0.5518(8)	0.2637(8)	4.1(3)
C4	0.560(1)	0.9606(8)	0.2949(7)	3.5(3)	C20	0.315(1)	0.6361(8)	0.3812(7)	3.6(3)
C5	0.515(1)	0.8545(8)	0.3079(7)	3.5(3)	C21	0.151(1)	0.6130(8)	0.3909(7)	4.0(3)
C6	0.352(1)	0.8169(8)	0.3176(7)	3.4(3)	C22	0.139(1)	0.6696(8)	0.5068(8)	4.7(3)
C7	0.233(1)	0.7035(8)	0.1832(7)	3.4(3)	C23	-0.007(1)	0.6549(9)	0.5251(8)	5.6(3)
C8	0.200(1)	0.7489(8)	0.0795(7)	3.3(3)	C24	-0.149(1)	0.5786(9)	0.4179(9)	5.4(3)
C9	0.312(1)	0.7647(9)	0.0232(8)	4.4(3)	C25	-0.137(1)	0.5221(9)	0.3040(8)	4.7(3)
C10	0.279(1)	0.8181(9)	-0.0623(8)	5.5(3)	C26	0.008(1)	0.5340(9)	0.2864(7)	4.6(3)

t,a,t-DCM (Major)

Atom	x	y	z	B(Å^2)	Atom	x	y	z	B(Å^2)
O1	0.5304(3)	0.1665(1)	0.7626(3)	4.41(7)	C12	0.4148(4)	0.1697(2)	0.7508(3)	2.92(9)
O2	0.3477(3)	0.2141(1)	0.7999(2)	3.98(7)	C13	0.4282(5)	0.2603(2)	0.8803(5)	6.3(1)
O3	0.1347(3)	0.1019(1)	0.8721(2)	4.10(7)	C14	0.4314(4)	0.0303(2)	0.8074(3)	2.66(9)
O4	0.3456(3)	0.0978(1)	0.9705(2)	4.37(7)	C15	0.2475(4)	0.0889(2)	0.8768(3)	2.95(9)
N1	0.0881(3)	0.1723(1)	0.5994(3)	3.13(8)	C16	0.3099(5)	0.1257(2)	1.0789(4)	6.6(1)
N2	0.5296(3)	0.0065(2)	0.8367(3)	4.04(9)	C17	0.3917(4)	0.1477(2)	0.4785(3)	2.44(9)
C1	0.3188(3)	0.1197(2)	0.6775(3)	2.13(8)	C18	0.2844(4)	0.1710(2)	0.3954(3)	3.2(1)
C2	0.3780(3)	0.0933(2)	0.5689(3)	2.14(8)	C19	0.2999(4)	0.2225(2)	0.3179(4)	4.5(1)
C3	0.3010(3)	0.0343(2)	0.5097(3)	2.16(8)	C20	0.4229(5)	0.2488(2)	0.3214(4)	5.6(1)
C4	0.3157(4)	0.0164(2)	0.3920(3)	2.82(9)	C21	0.5279(4)	0.2249(2)	0.3995(4)	5.4(1)
C5	0.2474(4)	-0.0359(2)	0.3326(3)	3.4(1)	C22	0.5141(4)	0.1743(2)	0.4794(4)	4.1(1)
C6	0.1609(4)	-0.0702(2)	0.3882(4)	3.3(1)	C23	0.1947(4)	-0.0493(2)	0.7745(3)	3.0(1)
C7	0.1481(4)	-0.0537(2)	0.5049(3)	2.97(9)	C24	0.1020(4)	-0.0549(2)	0.8479(4)	4.9(1)
C8	0.2186(3)	-0.0024(2)	0.5680(3)	2.25(8)	C25	0.1022(5)	-0.1088(2)	0.9231(4)	7.2(1)
C9	0.1976(3)	0.0119(2)	0.6974(3)	2.34(9)	C26	0.1939(6)	-0.1565(2)	0.9241(4)	7.3(2)
C10	0.2999(4)	0.0614(2)	0.7662(3)	2.28(8)	C27	0.2855(5)	-0.1528(2)	0.8499(4)	5.3(1)
C11	0.1874(4)	0.1499(2)	0.6339(3)	2.12(8)	C28	0.2856(4)	-0.0988(2)	0.7756(4)	3.8(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

count obtained in rapid pre-scans of each reflection. A somewhat wider scan width than normal had to be used since the sample exhibited a rather high mosaic spread as measured by the peak widths at half height. All of the crystals of this compound were noted visually to have extensive internal cracks and so the low quality was not surprising. Two standard reflections were monitored periodically during the course of the data collection as a check of crystal stability and electronic reliability, and these did not vary significantly. In reducing the data, Lorentz and polarization factors were applied, however no correction for absorption was made due to the small absorption coefficient. The structure was solved by MULTAN[60], which revealed the positions of the chlorine atoms. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinements was followed, after which all hydrogens were entered in ideally calculated positions and held fixed. Hydrogen temperature factors were estimated based on the thermal motion of the associated carbons. After all shift/esd ratios were less than 0.1, convergence was reached at the agreement factors listed in Table 12. No unusually high correlations were noted between any of the variables in the last cycle of least squares refinement and the final difference density map showed no peaks greater than 0.40 eÅ^{-3}. All calculations were made using Molecular Structure Corporation's TEXRAY 230 modifications of the SDP-PLUS series of programs. The final atomic coordinates are included in Table 13.

t,a,t-DCM (Major DMCF/c-DBC Adduct): A large clear colorless prismatic column of dimensions 0.55 × 0.25 × 0.15 mm was investigated as above. The Laue symmetry was determined to be $2/m$, and from the systematic absences noted the space group was shown unambiguously to be $P2_1/n$. Intensities were measured with the $\Theta-2\Theta$ scan technique. The structure was solved by MULTAN[60] which revealed the positions of 28 of the 34 non-hydrogen atoms in the molecule. After all shift/esd ratios were less than 0.1, convergence was reached at the agreement factors listed in Table 12. No unusually high correlations were noted between any of the variables in the last cycle of least squares refinement, and the final difference density map showed no peaks greater then 0.20 eÅ^{-3}. The final atomic coordinates are listed in Table 13.

CAS Registry Numbers

c-DBC: 6894-86-6 / *t*-DBC: 964-46-5 / TCNE: 670-54-2 / CA: 118-75-2 / CA$^{-\cdot}$: 17217-66-2 / *c*-DBC$^{+\cdot}$: 110658-00-9 / *t*-DBC$^{+\cdot}$: 11658-01-0 / *t*-DTT: 7058-83-5 / *c*-DTT: 6894-75-3 / *c*-DCM: 110569-28-3 / *t,a,t*-DCM: 110569-29-4 / *t,s,t*-DCM: 110569-30-7 / *t*-DBP: 110569-31-8 / *c*-DBP: 110569-32-9 / DMCF: 35234-87-8 / BC: 694-87-1 / AcOBC: 3469-03-2 / MeOBC: 36101-23-2 / MeOPhBC: 110569-35-2 / PhBC: 55190-64-2 / *t*-DBC · TCNE (EDA complex): 110569-33-0 / *c*-DBC · TCNE (EDA complex): 110569-34-1 / chloranil · hexamethylbenzene (EDA complex): 850-23-7 / chloranil · durene (EDA complex): 2473-78-1 / chloranil · *o*-xylene (EDA complex): 2473-75-8 / 2,2,3,3-tetracyano-1-methoxytetralin: 110569-36-3 / 2,2,3,3-tetracyano-1-(4-methoxyphenyl)-tetralin: 110569-37-4 / 2,2,3,3-tetracyano-1-phenyltetralin: 110569-38-5

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[35] [35a] Compare with the difference in the chemical shifts of the pair of tertiary hydrogens in the *cis*- and *trans*-adducts of DBC with tetracyanoethylene above. – [35b] For ambiguity owing to the additional resonance at 6.62, see Experimental Section.
[36] [36a] For example, compare the relative absorbances of CA and [CA,durene] in Figure 3B. – [36b] 1,2-Diphenylbenzocyclobutene is expected to be a slightly better electron donor than benzocyclobutene and about the same as *o*-xylene. Compare Figure 1 and the discussion following.
[37] Note also that cycloaddition arising from the CT excitation of the EDA complexes are not significant owing to low absorbances

at the concentrations of diphenylbenzocyclobutenes and DMCF or TCNE used in these studies[36].

[38] The photochemical results with the *trans*-isomer include a component from the competition from a slow *thermal* reaction with DMCF (which is slower than that with TCNE).

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[45] [45a] The high quantum yields in Tables 2 and 3 indicate that ring-opening of $DBC^{+\bullet}$ effectively competes with back electron transfer which is expected to be rapid. – [45b] See E. Haselbach, T. Bally, Z. Lanyiova, *Helv. Chim. Acta* **62** (1979) 577; B. Bischof, *J. Am. Chem. Soc.* **99** (1977) 8145; N. L. Bauld, J. Cessac, *ibid.* **99** (1977) 23.

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[48] We judged from the anodic peak potential (irreversible) of DBC at $E_p \approx 1.8$V vs SCE that the driving force and hence rate of back electron transfer is rapid.[22b]

[49] [49a] It is also possible but not likely (vide infra) that back electron transfer from the contact-ion pair $[DBC^{+\bullet}, TCNE^{-\bullet}]$ is so exergonic as to form the neutral *o*-xylylene directly. – [49b] For example for various types of photo-induced Diels-Alder condensations see D. P. Kjell, R. S. Sheridan, *J. Photochem.* **18** (1985) 205; G. Kaupp, R. Dyllick-Brenzinger, I. Zimmermann, *Angew. Chem., Int. Ed. Engl.* **14** (1975) 491; Angew. Chem. **87** (1975) 520; J. Saltiel, R. Dabestani, K. S. Schanze, D. Trojan, D. E. Townsend, V. L. Goedken, *J. Am. Chem. Soc.* **108** (1986) 2674; J. Mloch, E. Steckhan, *Angew. Chem. Int. Ed. Engl.* **24** (1985) 412; *Angew. Chem.* **97** (1985) 429; N. C. Yang, R. L. Yates, J. Masnovi, D. M. Shold, W. Chiang, *Pure Appl. Chem.* **51** (1979) 173; M. Dern, H. G. Korth, G. Kopp, R. Sustmaan, *Angew. Chem. Int. Ed. Engl.* **24** (1985) 337; *Angew. Chem.* **97** (1985) 324; K. Wilzbach, *J. Am. Chem. Soc.* **93** (1971) 2073.

[50] [50a] For the time-resolved kinetics of such loose ion pairs derived from a diffusional quenching, see J. D. Simon, K. S. Peters, *J. Am. Chem. Soc.* **103** (1981) 6403; J. L. Goodman, K. S. Peters, *ibid.* **108** (1986) 1700. – [50b] Loose ion pairs could also be formed from contact-ion pairs such as **I** in polar solvents[42]. The small (but discrete) amounts of rearrangement observed in acetonitrile (see Table 1, entry 9) may be such an example.

[51] For another example of the differences between contact and solvent-separated ion pairs, see R. M. Borg, R. O. Heuckeroth, A. J. Y. Lan, S. L. Quillen, P. S. Marino, *J. Am. Chem. Soc.* **109** (1987) 2728, 2738, and *Lecture at Symposium of Aspect Recents du Transfert Monoelectronique en Chimie Organique*, French Chemical Soc. Meeting, Lyon March 1987.

[52] Note that the formation of the cycloadduct *c*-DBP from *c*-DBC (eq. 13) represents such an isomerization. However the true extent of the isomerization in the isomeric *t*-DBC, as given in eq. 14, is obscured by competition from the thermal process (which is more facile than in *c*-DBC).

[53] The reduction potential of DMCF is expected to be more negative that of CA and thus disfavors eq. 31.

[54] For example, compare the magnitudes of the substituent constants in T. H. Lowry, K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, 2nd. Ed. Harper and Row, New York 1983.

[55] See C. Dass, M. L. Gross, *J. Am. Chem. Soc.* **103** (1983) 5724; G. S. Groenewold, E. K. Chess, M. L. Gross, *Org. Mass Spectrosc.* **19** (1984) 519, for leading refs.

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[58] Elemental analysis by Atlantic Microlabs, Atlanta, Ga.

[59] Further details and basic data concerning the X-ray analysis may be obtained from Fachinformationszentrum Energie Physik Methematik, D-7514 Eggenstein-Leopoldshafen (W. Germany), by specifying registry number CSD 52618, authors, and the reference to this publication.

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