

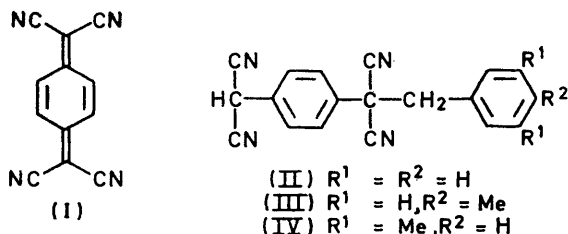
Photoaddition of the Charge-transfer Complexes of 7,7,8,8-Tetracyanoquinodimethane-Toluene Systems

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A novel photo-induced addition *via* charge-transfer excitation is described. Irradiation of a toluene solution of 7,7,8,8-tetracyanoquinodimethane gave α,α -dicyano-4-dicyanomethylbibenzyl. *p*-Xylene underwent similar addition on irradiation of its charge-transfer absorption band. The reaction was accelerated by the presence of trifluoroacetic acid or methanol, indicating the participation of a proton-transfer step. The yields of the photo-adducts were increased at higher temperatures. A mechanism involving an electron-transfer followed by a proton-transfer is proposed.

7,7,8,8-TETRACYANOQUINODIMETHANE (TCNQ) (I) is a typical electron acceptor and readily forms stable charge-transfer complexes or anion-radical derivatives with electron donors.¹ It has been reported that addition of tetrahydrofuran to TCNQ occurs on irradiation with sunlight or a sunlamp, and a radical mechanism has been proposed.² In previous papers we described a novel substitution of several charge-transfer complexes of 1,2,4,5-tetracyanobenzene (TCNB)-toluene derivatives on irradiation of their charge-transfer absorption bands.³ In continuing our studies on photochemical reactions of electron donor-acceptor systems, we investigated the TCNQ-toluene system and have found that a novel 1,6-photoaddition of toluene to TCNQ takes place upon irradiation in a similar manner as for TCNB-toluene complexes.⁴

Irradiation of a solution of TCNQ in toluene with a medium pressure mercury arc through a Pyrex filter for 10 h at room temperature gave the photoproduct (II) and a small amount of bibenzyl. Similarly when a solution of TCNQ in *p*-xylene was irradiated the product (III) was obtained. The TCNQ-mesitylene system reacted analogously when heated and (IV) was obtained.



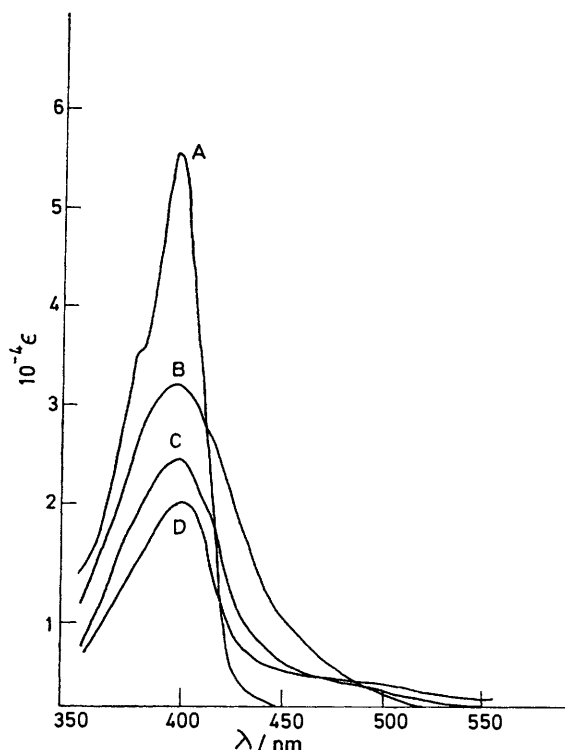
To clarify the first step of the reaction we examined the u.v. spectra of TCNQ in toluenes (Figure).

In TCNQ-toluene, a new absorption band was difficult to find, indicating that the charge-transfer interaction in the ground state is absent or weak. However, weak absorption bands due to neither the electron donor nor the electron acceptor appeared in the visible region as a tail of the absorption band of TCNQ in TCNQ-*p*-xylene and TCNQ-mesitylene systems and are regarded as charge-transfer bands.

¹ D. S. Acker and W. R. Hentler, *J. Amer. Chem. Soc.*, 1962, **84**, 3370, and subsequent papers.

² J. Diekman and C. J. Pedersen, *J. Org. Chem.*, 1963, **28**, 2879.

In order to demonstrate that the reaction was caused by irradiation within the charge-transfer band, irradiation of the TCNQ-*p*-xylene system with a glass-filtered high pressure mercury arc (500 W; $\lambda > 420$ nm)



U.v. spectra of TCNQ: A in acetonitrile, B in toluene, C in *p*-xylene, and D in mesitylene

under continuous heating was carried out to give (II) as the sole isolable product. This observation suggests that the excited state of the charge-transfer complex participates in the first step of the reaction.

Effects of Proton Donors.—Several examples of acid-catalysed photochemical reactions reported by Bryce-Smith and his co-workers have indicated that the use of proton donors such as trifluoroacetic acid or methanol

³ A. Yoshino, M. Ohashi, and T. Yonezawa, *Chem. Comm.*, 1971, 97.

⁴ Preliminary communication, K. Yamasaki, A. Yoshino, T. Yonezawa, and M. Ohashi, *J.C.S. Chem. Comm.*, 1973, 9.

can strongly influence the course of photochemical reactions which involve dipolar intermediates.⁵ Under the influence of these proton donors the dipolar intermediates give the products expected from a protonation-deprotonation sequence. Recent reports by the same authors indicate that the use of proton donor can also be used as a mechanistic probe for a proton-transfer step.^{6,7} We have found that in the presence of trifluoroacetic acid the photochemical substitution of toluene by TCNB was quenched, indicating the participation of a proton transfer step.^{3,4}

To test for the involvement of a proton-transfer step in the photoaddition of TCNQ to toluene, we repeated the reaction in the presence of 0.5M-trifluoroacetic acid: the rate of formation of the adduct (II) increased approximately ninefold, and a similar rate enhancement (fivefold) was obtained by the use of methanol. These results are analogous to those obtained in 1,4-photoaddition of amines to benzene⁷ and strongly indicate the importance of a proton-transfer step in the present reaction. The use of CH₃OD led to incorporation of one deuterium atom in the product in the amine-benzene systems,⁷ but in our case the deuterium from CF₃CO₂D was incorporated in the CH(CN)₂ group of (II) even in the dark, thus failing to provide direct proof for the participation of the proton in the proton donor.

Temperature Effects.—Only a few studies of the temperature dependence of photoreactions have been made at present.⁸ Bryce-Smith and his co-workers have pointed out that an increase in temperature will increase the yield, up to a point, in the photoaddition of maleic anhydride to benzene.⁹ We found that the chemical yields of the photoadducts (II) and (III) increased with temperature (Table). The same trend has been observed in the type II photoelimination of butyrophenone.¹⁰ This temperature dependence can be ascribed to the energy barrier involved in the photoaddition.

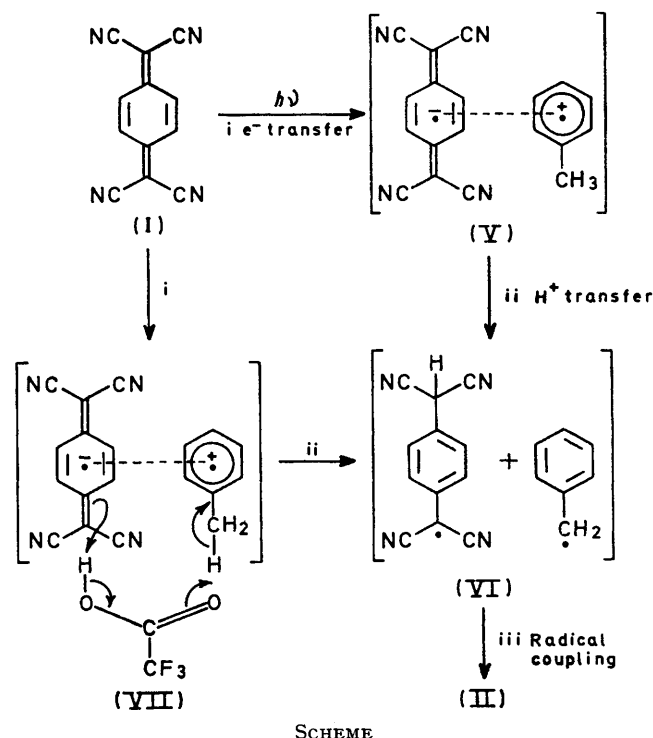
Temperature dependence of the yields of (II) and (III)

System	Irradiation temperature (°C)	Product	Yield (%)
TCNQ-Toluene	Ambient	(II)	16
	70–80	(II)	34
	110–120	(II)	67
TCNQ- <i>p</i> -Xylene	Ambient	(III)	3
	70–80	(III)	15
	110–120	(III)	20

Mechanism.—On the basis of the foregoing observations, we propose the mechanism shown in the Scheme for the reaction.

After excitation of the ground state complex (step i), a radical-cation–radical-anion pair (V), a charge-transfer exciplex, will be formed. Such radical pairs have been proposed by several authors, and there is ample evidence

for their existence.¹¹ In this pair (V) a proton from the toluene radical-cation shifts to the TCNQ radical-anion, producing the free radical pair (VI) (step ii) which then



collapses to the adduct (II) (step iii). The temperature effect mentioned above indicates that the rate-determining step in the overall reaction sequence will be the proton-transfer (step ii) or the radical coupling process (step iii).

Step ii has been included to account for the abnormal increase in the rate of adduct formation in the presence of proton donors. It seems reasonable to assume that trifluoroacetic acid would synchronously protonate the TCNQ radical-anion and deprotonate the toluene radical-cation (VII) in the process. The same role is also expected for methanol, as has already been proposed by Bryce-Smith.⁷ In the presence of trifluoroacetic acid the photochemical substitution of TCNB–toluene complexes is quenched,⁴ and the difference in behaviour displayed by trifluoroacetic acid in these two systems is still obscure. Nevertheless, these facts seem to indicate that the most important step of the photo-induced reactions of these charge-transfer systems must be the proton-transfer step.

There are many examples of substitution or addition reactions of charge-transfer complexes which take place in the ground state.¹² The TCNQ–mesitylene system

⁹ H. F. J. Augus and D. Bryce-Smith, *J. Chem. Soc.*, 1960, 4791.

¹⁰ G. J. Kavarnos and N. J. Turro, *Mol. Photochem.*, 1970, 2, 73.

¹¹ Y. Achiba, S. Katsumata, and K. Kimura, *Chem. Phys. Letters*, 1972, 213; M. Shimada, H. Masuhara, and N. Mataga, *ibid.*, p. 364.

¹² R. Foster, 'Organic Charge-transfer Complexes,' Academic Press, London, 1969, ch. 11.

⁵ D. Bryce-Smith, R. Deshpande, A. Gilbert, and J. Grzonka, *Chem. Comm.*, 1970, 561.

⁶ D. Bryce-Smith and G. B. Cox, *Chem. Comm.*, 1971, 915.

⁷ D. Bryce-Smith, M. T. Clarke, A. Gilbert, K. Klunklin, and C. Manning, *Chem. Comm.*, 1971, 916.

⁸ H. E. Zimmerman and W. R. Elser, *J. Amer. Chem. Soc.*, 1969, 91, 887; P. de Mayo, *Accounts Chem. Res.*, 1971, 4, 41.

is such a system and it is not obvious whether the reaction proceeds by the same mechanism as the photo-induced addition mentioned here. The TCNQ-mesitylene system must be included in the same class as the 2,6-dichloro-5,6-dicyano-*p*-benzoquinone-methylbenzenes¹³ or DDQ-triethylamine¹⁴ systems.

EXPERIMENTAL

G.l.c. analyses were performed with a Shimadzu GC-4A PTF machine with flame-ionisation detectors. I.r. spectra were recorded on a Hitachi 215 instrument and u.v. spectra on a Hitachi EPS-3T recording spectrophotometer. N.m.r. spectra were measured in CD₃CN on a Varian 220 instrument. M.p.s were measured on a hot stage apparatus. Elemental analyses were performed in the Kyoto University Microanalytical Centre. All reagents and solvents were reagent grades and were recrystallised or distilled before use.

Photolysis of 7,7,8,8-Tetracyanoquinodimethane (TCNQ) in Toluene.—A solution of TCNQ (150 mg) in toluene (85 ml) was irradiated for 10 h under nitrogen with a 100 W medium pressure mercury lamp through a Pyrex filter at reflux temperature. The solvent was then removed *in vacuo* at 40°. The residue was chromatographed on silica gel. Elution with benzene gave bibenzyl (36 mg), identified by comparison of its i.r. spectrum with that of an authentic sample. Further elution gave unchanged TCNQ (14 mg) and α,α -dicyano-4-dicyanomethylbibenzyl (II) (100 mg). Recrystallisation from benzene-petroleum (1:1) gave an analytical sample, m.p. 164–165°; ν_{\max} (KBr) 2250, 842, 780, and 698 cm⁻¹, τ (CD₃CN) 2.34 (4H, s), 2.61–2.77 (5H, m), 4.38 (1H, s), and 6.54 (2H, s), *m/e* 296 (*M*⁺) and 205 (*M*⁺ – CH₂Ph) (Found: C, 77.2; H, 4.05; N, 18.8. C₁₉H₁₂N₄ requires C, 77.1; H, 4.1; N, 18.9%).

Photolysis of TCNQ in p-Xylene.—A solution of TCNQ (300 mg) in *p*-xylene (300 ml) was irradiated with a 200 W medium pressure mercury lamp under a nitrogen atmosphere for 11 h. After removal of the solvent the residue was chromatographed on silica gel. Elution with benzene gave *p,p'*-dimethylbibenzyl (trace) whose i.r. spectrum was identical with that of an authentic sample. Further elution gave α,α -dicyano-4-dicyanomethyl-4'-methylbibenzyl (III) as needles (155 mg, 33%). Recrystallisation from benzene-petroleum (1:1) afforded an analytical sample, m.p. 172–173°, ν_{\max} (KBr) 2260, 2170, 842, and 824 cm⁻¹, τ (CD₃CN) 7.64 (3H, s), 6.43 (2H, s), 4.32 (1H, s), 2.80 (4H, s), and 2.27 (4H, s), *m/e* 310 (*M*⁺) and 205 (*M*⁺ –

CH₂C₆H₄CH₃) (Found: C, 77.4; H, 4.6; N, 18.2. C₂₀H₁₄N₄ requires C, 77.4; H, 4.55; N, 18.1%).

Thermal Reaction of TCNQ.—TCNQ (50 mg) was heated in toluene, *p*-xylene, or mesitylene (each 30 ml) at reflux temperature for 10 h. The solutions were then concentrated *in vacuo*. Treatment of toluene and *p*-xylene gave no product, only TCNQ being recovered quantitatively, whereas with mesitylene, concentration of the solution yielded a solid. Recrystallisation from benzene afforded α,α -dicyano-4-dicyanomethyl-3',5'-dimethylbibenzyl (IV) (72%), m.p. 152–153°, ν_{\max} (KBr) 2250, 2200, 800, and 717 cm⁻¹, τ (CD₃CN) 2.34 (4H, s), 2.96 (1H, s), 3.17 (2H, s), 4.35 (1H, s), 6.25 (2H, s), and 7.73 (6H, s), *m/e* 324 (*M*⁺) and 205 (Found: C, 77.5; H, 4.9; N, 17.3. C₂₁H₁₅N₄ requires C, 77.8; H, 4.95; N, 17.3%).

Limited Wavelength Experiment.—A solution of TCNQ (20 mg) in *p*-xylene was irradiated externally with a 500 W high pressure mercury arc under continuous heating for 40 h using a Toshiba 420 filter which removes the light with $\lambda < 420$ nm. The solution was evaporated to leave a solid which was chromatographed on silica gel. Elution with benzene gave (III) (72%, 22 mg).

Temperature Dependence Experiment.—A solution of TCNQ (50 mg) in toluene (30 ml) was irradiated for 10 h at room temperature, 70–80° (bath temperature), or 120–130°, respectively. The yields of (II) were determined by g.l.c. using tetramethyl pyromellitate as an internal standard. The same procedure was employed with *p*-xylene. The results are summarised in the Table.

Photolyses in the Presence of Proton Donors.—To a solution of TCNQ (50 mg) in toluene (30 ml) was added trifluoroacetic acid (28 mg) and the mixture was irradiated for 5 h at room temperature. After concentration of the solution the residue was analysed by g.l.c., giving the yield of (II) (78%). Under similar conditions irradiation of a solution without addition afforded (II) in 8% yield. When methanol was used instead of trifluoroacetic acid, (II) was obtained in 43% yield.

Treatment of Compound (II) with CF₃CO₂D.—To a mixture of (II) (54 mg) and toluene (21 ml) was added CF₃CO₂D (1.2 mg), and the mixture was kept at room temperature for 25 h in the dark. After evaporation of the volatile portion the residue was examined by n.m.r., and the peak at τ 4.38 [CH(CN)₂] had disappeared.

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¹³ R. Foster and I. Horman, *J. Chem. Soc. (B)*, 1966, 1049.

¹⁴ D. Buckley, S. Dunstan, and H. B. Henbest, *J. Chem. Soc.* 1957, 4880.