The Triplet-Triplet Absorption Spectra and Electronic Structures of Some Cyano-Substituted Benzenes

Hiroshi Morita, Satoru Matsumoto,* and Saburo Nagakura
The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato, Tokyo 106

(Received October 7, 1974)

Triplet-triplet (T–T) absorption bands were observed at 300, 297, and 320 nm for *m*- and *p*-dicyanobenzenes, and 1,3,5-tricyanobenzene, respectively. The nature of the observed spectra was investigated by calculating the wave functions of the triplet states and by analyzing them by the configuration analysis method. It was concluded that the T–T absorption bands of *m*- and *p*-dicyanobenzenes, and 1,3,5-tricyanobenzene correspond essentially to the transition from the locally (within the benzene ring) excited state to the intramolecular charge-transfer state.

Intramolecular charge-transfer (CT) interaction between the benzene ring and substituent groups is important to understand the electronic structures of some substituted benzene molecules. A large number of studies has hitherto been made on the effect of the interaction upon the singlet-singlet transition spectra of substituted benzenes and the intramolecular CT absorption characteristic of the interaction has been observed for various substituted benzene molecules.[1–10] Only a few studies, however, have been done on triplet-triplet transition spectra of substituted benzenes. Kimura and Tsubomura[11] studied theoretically the nature of the lowest triplet state for such substituted benzenes as phenol, anisole, aniline, *p*-phenylenediamine, and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD), paying special attention to the intramolecular CT character. Experimental studies have been made on the triplet-triplet absorption spectrum of the TMPD molecule.[12,13]

In the present study, in order to elucidate the electronic structures of the excited triplet states of benzonitrile (BN), *o*-, *m*-, and *p*-dicyanobenzenes (*o*-, *m*-, and *p*-DCNB), 1,3,5-tricyanobenzene (TRCNB), and 1,2,4,5-tetracyanobenzene (TCNB), we have measured their triplet-triplet (T–T) absorption spectra at 77 K and interpreted them with the aid of the configuration analysis[14] of the wave functions obtained by the Pariser-Parr-Pople SCF MO method[15,16] combined with the configuration interaction (CI) treatment.

Experimental

Commercially available *o*-, *m*-, and *p*-DCNB's of G.R. grade were purified by recrystallization from water, ethyl acetate, and methanol, respectively. TRCNB was prepared by the method described in the literature[17,18] and purified by recrystallization from methanol and thereafter from ethyl acetate. TCNB was purified by vacuum sublimation. Commercially available BN of G.R. grade was used without further purification.

The T–T absorption spectra were measured at 77 K in ethyl ether–isopentane (1 : 1) mixed solvent (EP). The samples were excited by a 500 W super-high-pressure mercury lamp. The details of the measurement were described in a previous paper.[19]

Theoretical

The π-electron structures of the ground and triplet excited states were calculated for all the molecules under consideration by taking the configuration interaction among all the singly excited configurations constructed from the Pariser-Parr-Pople SCF MO's.[15,16] The semi-empirical parameters chosen by Iwata *et al.*[20] for TCNB complexes were used for the present calculation. Electron paramagnetic resonance[21] and optical[22] studies of the lowest triplet states of benzene and methyl-substituted benzenes like toluene and mesitylene show that the geometrical structure of the benzene ring deviates from the hexagonal symmetry in the lowest triplet state. Slight distortion of the benzene ring from the hexagonal symmetry is also expected for the triplet states of the cyano-substituted benzene molecules under consideration. Because of the lack of the quantitative knowledge on the geometrical structures of their lowest triplet states, however, we assume in the present calculations that the molecules are planar and their benzene rings are of the hexagonal symmetry. The bond lengths are taken as follows; 1.39 Å for the C–C bond in the benzene ring, 1.46 Å for the C–C bond between the benzene ring and the substituent group, and 1.16 Å for the C≡N bond in the cyano group.

The wave functions obtained for some triplet states and the ground states of *m*- and *p*-DCNB's and TRCNB were analyzed with the aid of the configuration analysis method.[14] In the analysis, MO's of the benzene ring and those of the substituent groups were taken as the reference MO's. This choice of the reference MO's is appropriate to elucidate the intramolecular CT and locally excited (LE) characters for the triplet states of *m*- and *p*-DCNB's and TRCNB. In order to obtain the satisfactory convergence in the configuration analysis, it is necessary to take doubly excited configurations in addition to the singly excited ones.

Results and Discussion

As is shown in Fig. 1, the T–T absorption bands were observed at 300, 297, and 320 nm for *m*-DCNB, *p*-DCNB, and TRCNB, respectively. We measured the T–T absorption in the region 290~700 nm. But we

---

* Present address: Pioneering Research and Development Laboratories, Toray Industries, Inc., Sonoyama, Otsu, Shiga 520.

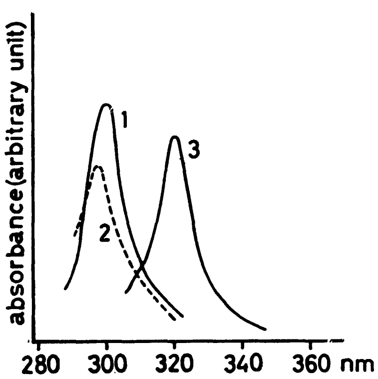

Fig. 1. T-T absorption spectra observed with (1) *m*-DCNB, (2) *p*-DCNB, and (3) TRCNB in EP solutions at 77 K.

could observe no band in the longer wavelength region for the respective molecules. Therefore, the observed bands are the longest wavelength band for the respective molecules. The observed T-T transition energies are listed in Table 1. We could observe no T-T absorption band for BN and *o*-DCNB in the wavelength region available in the present experiment. Concerning TCNB, we could not obtain any conclusive result on the T-T absorption.[23]

Table 1. The T-T transition energies (ΔE) and oscillator strengths (f) obtained experimentally and theoretically for benzene, BN, *o*-, *m*-, and *p*-DCNB's, TRCNB, and TCNB

	Obsd	Calcd		
	ΔE(eV)	ΔE(eV)	f	Upper state
Benzene	2.88[a]	2.91	0.000	T_4[d]
	5.36[b]	5.49	0.180×2	T_5[d]
	(∼5.17)[c]			
BN		4.52	0.498	T_8
o-DCNB		4.56	0.494	T_9
		4.59	0.138	T_{10}
m-DCNB	4.13	4.38	0.425	T_9
p-DCNB	4.17	4.22	0.783	T_9
TRCNB	3.87	4.27	0.228×2	T_7[d]
TCNB	(3.87)[e]	4.01	0.625	T_{11}

a) See Ref. 26. b) See Ref. 27. c) See Ref. 28. d) Degenerate upper state. e) See Ref. 23.

In Table 2, the calculated T-T transition energies and oscillator strengths of *m*-DCNB, *p*-DCNB, and TRCNB are tabulated. From the comparison between the observed and calculated transition energies and absorption intensities, the observed T-T absorption bands of *m*-DCNB, *p*-DCNB, and TRCNB are safely assigned to the transitions to the T_9, T_9, and degenerate T_7 states, respectively.

The triplet states of benzene, BN, *o*-DCNB, and TCNB were also calculated. The calculated transition energies of the T-T absorption bands that are expected to appear with considerable intensities in the longest wavelength region are tabulated in Table 1, together with the results of *m*- and *p*-DCNB's and TRCNB. The transition energies of benzene were calculated to be 2.91 and 5.49 eV for the transitions to the $^3E^+_{2g}$ and $^3E^-_{2g}$ states, respectively. These calculated values agree well with the observed values, 2.88 and 5.36 (or ∼5.17) eV.[26–28] This agreement seems to show the validity of the present calculation and to support the assignment of the T-T absorption bands observed with *m*- and *p*-DCNB's and TRCNB. The transitions to the T_8 state of BN and the T_9 and T_{10} states of *o*-DCNB are theoretically expected to be observed with considerable intensity near 4.5 eV (∼270 nm): this is consistent with the experimental fact that no corresponding bands were observed at wavelengths greater than 290 nm.

As shown in Table 1, the T-T transition energies of the substituted benzenes under consideration are calculated to be at least 1 eV smaller than that of benzene. This is due to the interaction between the locally excited and intramolecular CT (between the substituent group and the benzene ring) configurations. In order to clarify the situation in more detail, the results of the configuration analysis for the T_1 and T_9 states of *m*- and *p*-DCNB's are tabulated in Table 3 and those for the T_1 and T_7 states of TRCNB are tabulated in Table 4. In these tables, the results of the ground states of the respective compounds are

Table 2. The T-T transition energies (ΔE) and oscillator strengths (f) calculated for *m*-DCNB, *p*-DCNB, and TRCNB

Transition	*m*-DCNB		*p*-DCNB		TRCNB	
	ΔE(eV)	f	ΔE(eV)	f	ΔE(eV)	f
$T_2 \leftarrow T_1$	0.66	0.000	0.86	0.000	0.76[a]	0.000
$T_3 \leftarrow T_1$	1.13	0.000	1.07	0	1.44	0
$T_4 \leftarrow T_1$	1.37	0	1.29	0	1.46[a]	0.000
$T_5 \leftarrow T_1$	1.53	0.000	1.74	0	1.86	0
$T_6 \leftarrow T_1$	1.94	0.000	2.06	0	3.06[a]	0.003×2
$T_7 \leftarrow T_1$	2.97	0.001	2.86	0.000	4.27[a]	0.228×2
$T_8 \leftarrow T_1$	3.14	0.002	3.27	0.004	5.07	0
$T_9 \leftarrow T_1$	4.38	0.425	4.22	0.783	5.25[a]	0.104×2
$T_{10} \leftarrow T_1$	4.63	0.104	4.81	0.004	5.42	0
$T_{11} \leftarrow T_1$	5.07	0.038	5.00	0	5.68[a]	0.015×2

a) Degenerate upper state.

Table 3. The results of the configuration analysis (weights) obtained for the ground, T_1, and T_9 states of *m*- and *p*-DCNB's

Group	*m*-DCNB			*p*-DCNB		
	G	T_1	T_9	G	T_1	T_9
G^0	0.6945			0.6934		
A	0.0006	0.4688	0.2166	0.0005	0.4412	0.1762
A′		0.0001			0.0002	0.0001
A+B		0.1120	0.0846		0.1067	0.0778
B	0.1502	0.1564	0.0498	0.1508	0.1724	0.0774
B′		0.0169	0.0053		0.0187	0.0080
(Total from G^0 and LE configurations)	(0.8453)	(0.7542)	(0.3563)	(0.8447)	(0.7392)	(0.3395)
C	0.0716	0.0624	0.3276	0.0708	0.0710	0.3488
C+A		0.0368	0.0184		0.0324	0.0136
C+B		0.0298	0.0626		0.0332	0.0752
C′		0.0030	0.0170		0.0036	0.0082
(Total from CT_1 configurations)[a]	(0.0716)	(0.1320)	(0.4256)	(0.0708)	(0.1402)	(0.4458)
D	0.0418	0.0506	0.1516	0.0430	0.0588	0.1600
D+A		0.0231	0.0108		0.0202	0.0080
D+B		0.0102	0.0228		0.0116	0.0214
D′		0.0015	0.0044		0.0017	0.0022
(Total from CT_2 configurations)[b]	(0.0418)	(0.0854)	(0.1896)	(0.0430)	(0.0923)	(0.1916)
Total	0.9587	0.9716	0.9715	0.9585	0.9717	0.9769

a) CT configurations from the benzene ring to the cyano groups. b) CT configurations from the cyano groups to the benzene ring.

Table 4. The results of the configuration analysis (weights) obtained for the ground, T_1, and T_7 states of TRCNB

Group	G	T_1	T_7
G^0	0.5781		
A	0.0009	0.3784	0.1801
A′		0.0002	0.0001
A+B	0.0066	0.1389	0.1059
B	0.1890	0.1338	0.0526
B′	0.0258	0.0291	0.0113
(Total from G^0 and LE configurations)	(0.8004)	(0.6804)	(0.3500)
C	0.0879	0.0586	0.2359
C+A		0.0458	0.0234
C+B	0.0240	0.0393	0.0778
C′	0.0052	0.0057	0.0249
(Total from CT_1 configurations)[a]	(0.1171)	(0.1494)	(0.3620)
D	0.0530	0.0487	0.1517
D+A		0.0289	0.0139
D+B	0.0143	0.0186	0.0409
D′	0.0016	0.0022	0.0095
(Total from CT_2 configurations)[b]	(0.0689)	(0.0984)	(0.2160)
Total	0.9864	0.9282	0.9280

a) CT configurations from the benzene ring to the cyano groups. b) CT configurations from the cyano groups to the benzene ring.

also given for the purpose of comparison. In these tables, G^0 denotes the ground configuration, and Groups A and A′ represent the singly and doubly excited LE configurations in the benzene ring, respectively; Groups B and B′, the singly and doubly excited LE configurations in the substituent groups, respectively; Groups C and C′, the singly and doubly excited CT configurations from the benzene ring to the substituent groups, respectively; Groups D and D′, the singly and doubly excited CT configurations from the substituent groups to the benzene ring, respectively, and Group C+A, *etc.*, the doubly excited configurations composed of configurations in Groups C and A, *etc.*

As is clearly seen in Table 3, the results of the configuration analysis for *m*- and *p*-DCNB's are similar to each other; the ground singlet state (G) and the lowest triplet state (T_1) are mainly composed of the ground and LE configurations, while in the T_9 states, the contribution of the CT configurations is more predominant than that of the LE configurations. This shows that the observed T-T absorption bands of *m*- and *p*-DCNB's correspond to the transition from the LE state to the intramolecular CT state.

Concerning *p*-DCNB, the contribution of the CT configurations in Group C may increase the double bond character of the C-C bonds between the benzene ring and the cyano groups. Hence, the molecular geometry may tend towards a quinoid structure. In actuality, this tendency was observed by Hirota[29] from the measurement of the spin densities in the T_1

state of *p*-DCNB.

As is seen in Table 4, the nature of the T-T absorption band of TRCNB is analogous to that of *m*- and *p*-DCNB's. The T-T absorption bands of BN, *o*-DCNB, and TCNB listed in Table 1 also correspond to the transition from the LE state to the intramolecular CT state.

References

1) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); S. Nagakura, *ibid.*, **23**, 1441 (1955).

2) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.* (London), **A68**, 601 (1955); J. N. Murrell, *ibid.*, **A68**, 969 (1955); *Tetrahedron, Suppl.* **2**, **19**, 277 (1963).

3) T. E. Peacock, *Mol. Phys.*, **3**, 453 (1960).

4) J. E. Bloor, *Canad. J. Chem.*, **39**, 2256 (1961); J. E. Bloor and F. Peradejordi, *Theor. Chim. Acta*, **1**, 83 (1962).

5) I. Fischer-Hjalmars, *Ark. Fys.*, **21**, 123 (1962).

6) S. Nagakura, *Pure* and *Appl. Chem.*, **7**, 79 (1963).

7) J. Tanaka, This Bulletin, **36**, 833 (1963).

8) S. Nagakura, M. Kojima, and Y. Maruyama, *J. Mol. Spectrosc.*, **13**, 174 (1964); K. Tabei and S. Nagakura, This Bulletin, **38**, 965 (1965).

9) K. Kimura, H. Tsubomura, and S. Nagakura, *ibid.*, **37**, 1336 (1964).

10) K. Kimura and S. Nagakura, *Mol. Phys.*, **9**, 117 (1965).

11) K. Kimura and H. Tsubomura, *ibid.*, **11**, 349 (1966).

12) H. Tsubomura, N. Yamamoto, and Y. Nakato, This Bulletin, **39**, 1092 (1966); N. Yamamoto, Y. Nakato, and H. Tsubomura, *ibid.*, **39**, 2603 (1966).

13) K. D. Cadogan and A. C. Albrecht, *J. Phys. Chem.*, **73**, 1868 (1969).

14) H. Baba, S. Suzuki, and T. Takemura, *J. Chem. Phys.*, **50**, 2078 (1969).

15) R. Pariser and R. G. Parr, *ibid.*, **21**, 466, 767 (1953).

16) J. A. Pople, *Proc. Roy. Soc.* (London), **A68**, 81 (1955).

17) G. M. Bennet and R. L. Wain, *J. Chem. Soc.*, **1936**, 1108.

18) A. S. Bailey, B. R. Henn, and J. M. Langdon, *Tetrahedron*, **19**, 161 (1963).

19) S. Matsumoto, S. Nagakura, S. Iwata, and J. Nakamura, *Mol. Phys.*, **26**, 1465 (1973).

20) S. Iwata, J. Tanaka, and S. Nagakura, *J. Amer. Chem. Soc.*, **88**, 894 (1966).

21) M. S. de Groot and J. H. van der Waals, *Mol. Phys.*, **6**, 545 (1963); M. S. de Groot, I. A. M. Hesselmann, and J. H. van der Waals, *ibid.*, **10**, 91 (1965); *ibid.*, **13**, 583 (1967).

22) G. C. Nieman and D. S. Tinti, *J. Chem. Phys.*, **46**, 1432 (1967); G. C. Nieman, *ibid.*, **50**, 1674 (1969).

23) A weak band was observed for TCNB around 320 nm. Since the TCNB molecule ionizes fast in the excited state,[24,25] it is not sure whether or not this band corresponds to the T–T absorption.

24) M. Sofue and S. Nagakura, This Bulletin, **38**, 1048 (1965).

25) H. Masuhara, M. Shimada, N. Tsujino, and N. Mataga *ibid.*, **44**, 3310 (1971).

26) R. Astier and Y. H. Meyer, *Chem. Phys. Lett.*, **3**, 399 (1969).

27) C. S. Burton and H. E. Hunziker, *ibid.*, **6**, 352 (1970).

28) T. S. Godfrey and G. Porter, *Trans. Faraday Soc.*, **62**, 7 (1966).

29) Private communication from Professor Noboru Hirota, State University of New York at Stony Brook.