Charge-Transfer Interaction and Molecular Arrangement in the Crystals of 2-(*p*-Nitrophenoxy)ethyl Ethers and Amines

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X-Ray crystallographic analysis of the Acceptor-$(CH_2)_2$-Donor type compounds, *p*-$O_2NC_6H_4OCH_2CH_2OAr$ (Ar=*m*- and *p*-$Me_2NC_6H_4$, and *m*-$Et_2NC_6H_4$) and *p*-$O_2NC_6H_4OCH_2CH_2N(CH_3)C_6H_4OMe$-*p*, has been carried out. Among these, only *m*-dimethylamino derivative (**1**) gives dark red prisms in which a close arrangement of the electron-donor and acceptor groups is observed. With regard to the central C–C bond in ArO–C–C–OAr′ or ArO–C–C–NAr′, three of the above-mentioned four compounds show *gauche* conformation: **1** is the exception. The preference of the *gauche*, probably characteristic of O–C–C–O (or –N) group, is suggested to be due to a small energy difference between the *trans* and *gauche* forms by using the MM2 and the PM3 approximation. Charge-transfer interaction energy in **1** as an intermolecular force is estimated to be barely large enough to make the *trans* conformation favorable over the *gauche*.

In order to furnish to an assembly of molecules specific physical and/or chemical properties that require a definite arrangement of molecules in a crystal, several intermolecular forces (such as hydrogen bond, electrostatic forces, dipole–dipole interaction, charge-transfer (CT) interaction, van der Waals force, etc.) are utilized to attain the designed structure. Recent advances in the area of electronic and magnetic properties of organic molecules have made it necessary to understand the significance and role of these forces. This paper is intended to analyze the role of one of such forces, CT interaction, in solid state by using an incidentally discovered compound showing CT absorption band and its analogues.

During the study of photochemical reactions between aromatic nitro and dimethylamino groups, we obtained a compound with *p*-nitrophenoxy and *m*-(dimethylamino)phenoxy groups bound together with an ethylene chain (**1**) that solidifies in dark-red crystals. On dissolving the compound in ethanol for recrystallization, a warm solution (concentration >ca.1.5 M, 1 M=1 mol dm^{-3}) showed red color, though a dilute solution is almost colorless and shows no extra electronic absorptions other than those corresponding to the composite chromophores. These findings suggest that there exists intermolecular CT interactions between the two aromatic moieties. Since the similar interaction phenomenon in solid state is not observed for an analogue having anilino moiety in place of (dimethylamino)phenoxy group as a donor, the difference seemed to be due at least partly to the electron-donating ability of the donor moiety, but it is also noteworthy that no other homologues of **1** ($n=3$ through 12) show the similar phenomenon; that is, the CT interaction was observed only for the $n=2$ homologue.

In the hope of finding some clues to the structural factors determining molecular arrangements in this solid, we have analyzed the crystal structure of **1** and, additionally, a group of compounds (**2** through **5**); *m*-diethylamino homologue (**2**) was chosen for comparison of the steric effects between methyl and ethyl groups, with the electronic effect maintained, and *p*-dimethylamino analogue (**3**) was for comparison of the position of dimethylamino group; derivatives of 1-(*N*-methyl-*p*-anisidino)-2-(*p*-nitrophenoxy)ethane (**4**) and 1-(*N*-methyl-*m*-anisidino)-2-(*p*-nitrophenoxy)ethane (**5**) were chosen in order to study the effect of replacing the atom attached to the ethylene chain, thus altering the direction of the dipole moment of the donor moiety (Chart 1).

Experimental

General. Melting points are uncorrected. ^{1}H NMR spectra were recorded on a Varian EM-390 spectrometer with TMS as an internal standard. Homogeneity of the compounds was established by HPLC on a JASCO 880-PU with a reverse phase column packed with Fine SIL C_{18}-5 using methanol as eluent.

1-[*m*-(Dimethylamino)phenoxy]-2-(*p*-nitrophenoxy)ethane (1). A mixture of 0.91 g (3.7 mmol) of 2-(*p*-nitrophenoxy)ethyl bromide,[1] 0.69 g (5.0 mmol) of *m*-dimethylaminophenol, 0.28 g (5.0 mmol) of potassium hydroxide, and 0.2 g of tetrabutylammonium bromide in 10 ml of 2-methoxyethanol was stirred at 100 °C for 2.5 h. The reaction mixture was poured into 5% aqueous sodium hydroxide solution and extracted with three 20-ml portions of chloroform. The extracts were collected and washed with 20 ml of water saturated with sodium chloride. Af-

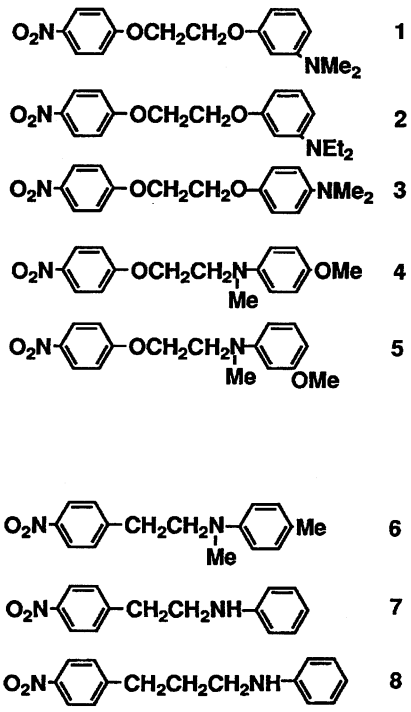

Chart 1.

ter drying over anhydrous magnesium sulfate, the solvent was removed by distillation; then the residue was charged on a chromatography column packed with silica gel. Elution with benzene–CH_2Cl_2 mixture (1 : 1) gave 0.63 g (56%) of dark red plates: Mp 116—117 °C; ^{1}H NMR (90 MHz, $CDCl_3$ + DMSO-d_6) δ=2.97 (s, 6H), 4.42—4.72 (m, 4H), 6.38—6.58 (m, 6H), 8.40 (d, J=9.6 Hz, 2H).

Found: C, 63.46; H, 5.97; N, 9.24%. Calcd for $C_{16}H_{18}N_2O_4$: C, 63.56; H, 6.00; N, 9.27%.

1-[*m*-(Diethylamio)phenoxy]-2-(*p*-nitrophenoxy)-ethane (2). A mixture of 0.49 g (2.0 mmol) of (*p*-nitrophenoxy)ethyl bromide, 0.33 g (2.0 mmol) of *m*-diethylaminophenol, 0.08 g (2.0 mmol) of sodium hydroxide, 0.05 g of tetrabutylammonium bromide, and 5 ml of water was stirred overnight (ca. 20 h) at 100 °C. After the usual workup, the crude solid was extracted with ethyl acetate. The solvent was removed by distillation from the combined extracts. Recrystallization of the residue from ethanol–benzene mixture gave 0.41 g (62%) of yellow needles: Mp 130—131 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ=1.10 (t, J=7 Hz, 6H), 3.31 (q, J=7 Hz, 4H), 4.34 (br. s, 4H), 6.0—7.1 (m, 4H), 6.96 (d, J=9 Hz, 2H), 8.16 (d, J=9 Hz, 2H).

Found: C, 65.53; H, 6.62; N, 8.71%. Calcd for $C_{18}H_{22}N_2O_4$: C, 65.44; H, 6.71; N, 8.48%.

2-(*p*-Nitrophenoxy)ethanol. A mixture of 3.58 g (20 mmol) of sodium *p*-nitrophenoxide dihydrate and 5.00 g (40 mmol) of 2-bromoethanol was stirred overnight at 100 °C. The mixture was washed with 5% aqueous NaOH solution and water, and extracted with CH_2Cl_2. After removing the solvent by distillation, the residue was recrystallized from benzene, yielding 2.86 g (73%) of 2-(*p*-nitrophenoxy)ethanol: Pale yellow needles, Mp 83—84 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ=2.23 (br. t, J=6 Hz, 1H), 3.8—4.3 (m, 4H), 6.96 (d, J=9 Hz, 2H), 8.23 (d, J=9 Hz, 2H).

Found: C, 52.65; H, 5.03; N, 7.56%. Calcd for $C_8H_9NO_4$: C, 52.46; H, 4.95; N, 7.65%.

2-[*p*-(Dimethylamino)phenoxy]ethanol. To a solution of 2.75 g (15 mmol) of 2-(*p*-nitrophenoxy)ethanol in 90 ml of ethanol was added 0.10 g of PtO_2. This mixture was stirred under hydrogen at room temperature until the absorption of the hydrogen stopped. To this reaction mixture, 5.00 g of ca. 37% aqueous formaldehyde and 0.1 ml acetic acid were added, and the mixture was further stirred under hydrogen at room temperature for 15 h. Each step of the reactions was monitored by HPLC. After the catalyst was removed by decantation and filtration, the ethanol solution was concentrated with a rotary evaporator. On standing, the residue gave 2.72 g (99%) of 2-[*p*-(dimethylamino)phenoxy]ethanol as pale red flakes; these were further purified by vacuum distillation with Kuhgelrohr: Mp 47—48 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ=2.85 (s, 6H), 3.8—4.1 (m, 4H), 6.5—7.0 (m, 4H).

Found: C, 66.21; H, 8.28; N, 7.48%. Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73%.

1-[*p*-(Dimethylamino)phenoxy]-2-(*p*-nitrophenoxy)ethane (3). To a stirred solution of 2.62 g (14.5 mmol) of 2-[*p*-(dimethylamino)phenoxy]ethanol in 25 ml of anhydrous DMF was added 0.58 g (14.5 mmol) of sodium hydride (60% dispersion in mineral oil) at room temperature under nitrogen, and after 30 min of stirring 2.05 g (14.5 mmol) of *p*-nitrofluorobenzene was added during 10 min. The stirring was continued at room temperature for 30 min and further for 1 h at 50—60 °C. After cooling, the mixture was poured into 150 ml of water and extracted with four 15-ml portions of CH_2Cl_2. The combined extracts were washed with three 15-ml portions of water and dried over anhydrous K_2CO_3. After the solvent was removed, recrystallization of the residue from ethanol–chloroform mixture gave 1.48 g (34%) of pale yellow plates: Mp 153—154 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ=2.88 (s, 6H), 4.31 (br. s, 4H), 6.6—7.1 (m, 4H), 6.97 (d, J=9 Hz, 2H), 8.16 (d, J=9 Hz, 2H).

Found: C, 63.61; H, 5.87; N, 9.42%. Calcd for $C_{16}H_{18}N_2O_4$: C, 63.56; H, 6.00; N, 9.27%.

***N*-[2-(*p*-Nitrophenoxy)ethyl]-*p*-anisidine.** A mixture of 1.23 g (5 mmol) of 2-(*p*-nitrophenoxy)ethyl bromide and 1.85 g (15 mmol) of *p*-anisidine was heated on a water-bath at 80—90 °C for 1 h. The mixture was poured into 50 ml of 10% aqueous sodium carbonate and extracted with CH_2Cl_2. After usual workup and recrystallization from carbon tetrachloride and ethanol, sublimation under vacuum gave 0.73 g (50%) of orange yellow needles: Mp 100—101 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ=3.59 (t, J=6 Hz, 2H), 3.77 (s, 3H), 4.13 (t, J=6 Hz, 2H), 6.56 (d, J=8 Hz, 2H), 6.81 (d, J=8 Hz, 2H), 6.96 (d, J=9 Hz, 2H), 8.12 (d, J=9 Hz, 2H).

Found: C, 62.54; H, 5.60; N, 9.76%. Calcd for $C_{15}H_{16}N_2O_4$: C, 62.49; H, 5.59; N, 9.72%.

1-(*N*-Methyl-*p*-anisidino)-2-(*p*-nitrophenoxy)ethane (4). A mixture of 0.289 g (1.0 mmol) of *N*-[2-(*p*-nitrophenoxy)ethyl]-*p*-anisidine, 0.145 g (1.1 mmol) of methyl iodide and 0.70 g of potassium carbonate in 5 ml of ethanol was stirred overnight at 60 °C. The reaction mixture was poured into 30 ml of water and extracted with three 15-ml portions of CH_2Cl_2. The combined extracts were dried over anhydrous potassium carbonate. After the solvent was removed by distillation, the residue was charged on

a chromatography column packed with alumina and eluted with benzene–dichloromethane mixture (1 : 1). Recrystallization of the first eluate from ethanol–benzene gave 0.189 g (63%) of orange needles: Mp 60—61 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ=2.98 (s, 3H), 3.71 (t, J=6 Hz, 2H), 3.76 (s, 3H), 4.20 (t, J=6 Hz, 2H), 6.75 (d, J=9 Hz, 2H), 6.85 (d, J=9 Hz, 2H), 6.92 (d, J=9 Hz, 2H), 8.17 (d, J=9 Hz, 2H).

Found: C, 63.37; H, 5.86; N, 9.43%. Calcd for $C_{16}H_{18}N_2O_4$: C, 63.56; H, 6.00; N, 9.27%.

1-(*m*-Anisidino)-2-(*p*-nitrophenoxy)ethane. A mixture of 0.61 g (2.5 mmol) of 2-(*p*-nitrophenoxy)ethyl bromide and 1.0 g (8.1 mmol) *m*-anisidine was heated at 100 °C for 1 h; this hot mixture was poured into 30 ml of 10% aqueous sodium carbonate solution. The suspension was extracted with three 10-ml portions of CH_2Cl_2; combined extracts were dried over anhydrous potassium carbonate. After removing the solvent by distillation, the residue was charged on a chromatography column packed with 40 g of alumina and eluted with benzene–dichloromethane mixture (1 : 1). Recrystallization of the first eluate from ethanol–benzene gave 0.67 g (93%) of yellow plates: Mp 97—98 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ=3.85 (t, J=5 Hz, 2H), 4.09 (s, 3H), 4.09 (br. s, 1H), 4.23 (t, J=5 Hz, 2H), 6.23 (t, J=2 Hz, 1H), 6.29 (dd, J=2 and 8 Hz, 1H), 6.32 (dd, J=2 and 8 Hz, 1H), 6.96 (d, J=9 Hz, 2H), 7.11 (t, J=8 Hz, 1H), 8.19 (d, J=9 Hz, 2H).

Found: C, 62.65; H, 5.46; N, 9.82%. Calcd for $C_{15}H_{16}N_2O_4$: C, 62.49; H, 5.59; N, 9.72%.

1-(*N*-Methy-*m*-anisidino)-2-(*p*-nitrophenoxy)ethane (5). A mixture of 0.289 g (1.0 mmol) of *N*-[2-(*p*-nitrophenoxy)ethyl]-*m*-anisidine, 0.145 g (1.1 mmol) of methyl iodide, and 0.70 g of potassium carbonate in 5 ml of ethanol was stirred overnight at 60 °C. To this 6 drops of methyl iodide and 1 ml of water was added and stirring was continued for 40 h in total. The reaction mixture was poured into 30 ml of water and extracted with three 15-ml portions of CH_2Cl_2. The combined extracts were dried over anhydrous potassium carbonate. After the solvent was removed by distillation, the residue was charged on a chromatography column packed with 45 g of alumina and eluted with benzene–dichloromethane mixture (3 : 1). The solvent was removed by distillation, then the remaining viscous liquid crystallized on standing, giving 0.175 g (58%) of pale yellow plates: Mp 42—43 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ=3.05 (s, 3H), 3.80 (s, 3H), 4.22 (br. t, J=6 Hz, 4H), 6.27—6.30 (m, 2H), 6.32 (dd, J=2 and 9 Hz, 1H), 6.38 (dd, J=3 and 8 Hz, 1H), 6.92 (d, J=9 Hz, 2H), 7.17 (t, J=8 Hz, 1H), 8.17 (d, J=9 Hz, 2H).

Found: C, 63.34; H, 6.05; N, 9.16%. Calcd for $C_{16}H_{18}N_2O_4$: C, 63.56; H, 6.00; N, 9.27%.

X-Ray Crystallography. X-Ray diffraction data were collected with graphite-monochromated Mo $K\alpha$ (λ= 0.071069 nm) radiation on a Rigaku AFC5 four-circular diffractometer. No absorption correction was applied to the data and the structure was solved by direct methods with SAPI-85[2] and other analytical calculations were performed by using UNICS-III program system[3] on PANAFACOM A-70 computer system. Hydrogen atoms were located from difference Fourier synthesis; block-diagonal least-squares refinement was carried out with isotropic and anisotropic thermal parameters for all hydrogen atoms and for all non-hydrogen atoms, respectively. X-Ray crystallographic analysis data are summarized in Table 1. Anisotropic thermal parameters, full listings of bond distances and angles, and calculated and observed structure factors are deposited as Document No. 68059 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Calculations. The molecular mechanics calculations were performed with the MM2 force field mounted on the Chem3D program (Cambridge Scientific Computing, Inc. version 3.1.2) using default parameters. The initial geometries of each compound were taken from their crystallographic analysis. Semi-empirical molecular orbital calculations were carried out with the PM3 approximation.[4]

Results and Discussion

X-Ray crystallographic analysis data for the compounds **1**, **2**, **3**, and **4** are summarized in Table 1. The compound **5** did not give a single crystal suitable for X-ray analysis, but from its pale yellow color, CT interaction was probably absent in the solid state. The crystal of **4** is obtained in thin plates and the number of the reflections is the smallest among the four compounds. Accordingly the R value is large, but the data are sufficiently reliable for the present discussion. The structures of the molecules in solid state, a pair for **1** and single molecules for **2**, **3**, and **4**, are shown in Figures 1, 2, 3, and 4, respectively. For compound **1**, the interatomic distances between the molecular pairs shorter than 0.36 nm are given in Table 2 along with charge densities on the corresponding atoms obtained by the PM3 approximation.

Charge-Transfer Interaction. As expected from spectral behavior in solution, the dark red color of the crystal of **1** is a reflection of the proximity of *m*-dimethylaminophenoxy and *p*-nitrophenoxy moieties; two molecules form a centrosymmetric head-to-tail pair and this pair in turn serves as a second constituent unit of the crystal (Fig. 1c). The donor and acceptor ring planes are not parallel with each other, but cross at an angle of 10.9° (Fig. 1b). As seen in Fig. 1a, which is drawn as a projection along the line through C_{15} and $O_{2'}$ (nitro oxygen) atoms, the overlapping area of the two aromatic rings is very small. For instance, the shortest interatomic distance in the pair molecules is 0.341 nm between C_{15} and $O_{2'}$ and not between the ring atoms. The next two nearest couples except for combinations including methyl carbon atom (C_{21}) are C_{11}–$C_{8'}$ (0.348 nm) and N_6–$N_{5'}$ (0.352 nm), and all the other combinations are more than 0.360 nm apart.

Several attempts have been reported to explain the origin of the arrangement of molecules in crystals.[5—7] For a CT complex consisting of 3,5-dinitrobenzamide moiety as an acceptor and 2-naphthylamine moiety as a donor,[8—10] theoretical estimation of interaction energy of CT complex was carried out by Topiol et al. with the AM1 approximation and ab initio method at the STO-3G level.[11] Using point-charge representations of the aromatic moieties, they have shown that the interaction energy calculated for scanning relative orien-

Table 1. Crystallographic Data for **1**, **2**, **3**, and **4**

Compounds	**1**	**2**	**3**	**4**
M. F.	$C_{16}H_{18}N_2O_4$	$C_{18}H_{22}N_2O_4$	$C_{16}H_{18}N_2O_4$	$C_{16}H_{18}N_2O_4$
M. W.	302.3292	330.3828	302.3292	302.3292
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/a$	$P2_1/n$
a/Å	15.242(3)	12.282(3)	17.052(2)	12.579(3)
b/Å	11.258(4)	12.734(3)	7.175(0)	12.934(3)
c/Å	9.017(3)	8.097(1)	12.189(2)	10.205(2)
α/°	90.0	102.62(2)	90.0	90.0
β/°	96.58(2)	89.93(2)	92.55(1)	111.79(2)
γ/°	90.0	133.97(1)	90.0	90.0
V/Å^3	1537(1)	868.8(4)	1489.9(3)	1541(1)
Z	4	2	4	4
D_{calcd}/g cm^{-3}	1.306	1.263	1.348	1.303
μ_{calcd}/cm^{-1}	0.886	0.839	0.915	0.884
Scan mode	$2\theta/\omega$	$2\theta/\omega$	$2\theta/\omega$	$2\theta/\omega$
2θ range/°	3.0—55.0	3.0—55.0	3.0—55.0	3.0—55.0
Scan speed/° min^{-1}	4 in 2θ	2 in 2θ	4 in 2θ	4 in 2θ
Scan width/°	1.2+0.15 tan θ	1.3+0.14 tan θ	1.1+0.14 tan θ	0.8+0.3 tan θ
Reflections measd.	2596	4320	3915	3498
Reflections included	1761 ($F>3\sigma$)	3112 ($F>2.5\sigma$)	2271 ($F>2.5\sigma$)	1163 ($F>2.5\sigma$)
Parameters refined	272	306	272	272
R[a)]	0.073	0.061	0.054	0.117
R_w[b)]	0.077	0.059	0.048	0.119

a) $R=\sum||F_o|-|F_c||/\sum|F_o|$. b) $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$ the weighting factor w was determined as the value of w $(|F_o|-|F_c|)^2$ takes constantly independently for $|F_o|$.

tation of the components reveals several energy minimum points including large π–π overlap geometries as well as less overlapped ones. The latter conformations, though less stable, are quite similar to the case observed in **1**. Since no hydrogen bond is possible between the geminate molecules and π–π overlap is slight, we suspected that the observed arrangement of the molecules might be due to strong electrostatic interaction. Hence we scrutinized the local interaction force with a simplified point-charge model; that is, electrostatic energy is assumed to be mainly dependent on the sum of the energies between the close atom pairs. Examination from the data in Table 2 shows that there exists strong electrostatic repulsion in the nearest pair C_{15}–$O_{2'}$ and moderate one in N_6–$N_{5'}$, which is insufficiently compensated by C_{11}–$C_{8'}$ and C_7–$C_{9'}$ attraction. In addition, steric repulsion including methyl (C_{21}) hydrogen atoms should be taken into consideration. These local electrostatic forces thus sum to repulsion or at least not to strong attraction and cannot be the major interaction forces contributing to the observed structure. In order to obtain more reliable data, overall atomic charges should be taken into account and a much more elaborate calculation, including not only electrostatic force but also π–π overlap interaction, should be applied. Since such an attempt is not promising,[11,12] we took no further step in theoretical considerations.

Table 2. Interatomic Distance (Less Than 0.36 nm) between the Acceptor and the Donor Moieties in **1**

Bond[a)]	PM3 Charge density		Distance/nm[b)]
Donor–Acceptor	Donor	Acceptor	
C_{15}–$O_{2'}$	−0.1897	−0.6069	0.3411(4)
C_{11}–$C_{8'}$	−0.2350	0.0385	0.3480(4)
C_{21}–$O_{4'}$		−0.6037	0.3515(4)
N_6–$N_{5'}$	0.0213	1.3150	0.3516(4)
C_{21}–$N_{5'}$		1.3150	0.3561(4)
C_7–$C_{9'}$	0.004	−0.4570	0.3570(4)
C_7–$C_{8'}$	0.004	0.0385	0.3593(4)

1) For assignment of the number of the atoms, see Fig. 1a. 2) The value in parentheses is standard deviation.

Replacement of the dimethylamino group with diethylamino results in disappearance of CT interaction (**2**). The bulkier ethyl group canot easily keep a similar arrangement of molecules to that in **1**, where the methyl carbon atom is at the distance of 0.352 nm apart from the nitro oxygen. Change of the position of dimethylamino group from *meta* to *para* (**3**) results in the disappearance of the interaction, even though a stronger electron-donor, *p*-dimethylaminophenyl ether moiety, might provide more favorable conditions than *m*-dimethylaminophenyl ether for the CT interaction. Alteration of the atom attached the ethylene chain from oxygen to nitrogen without changing the donor power (**4** and **5**), which corresponds to reversion of the dipole moment in the donor part, is again ineffective to induce CT interaction in the crystals. All these facts suggest

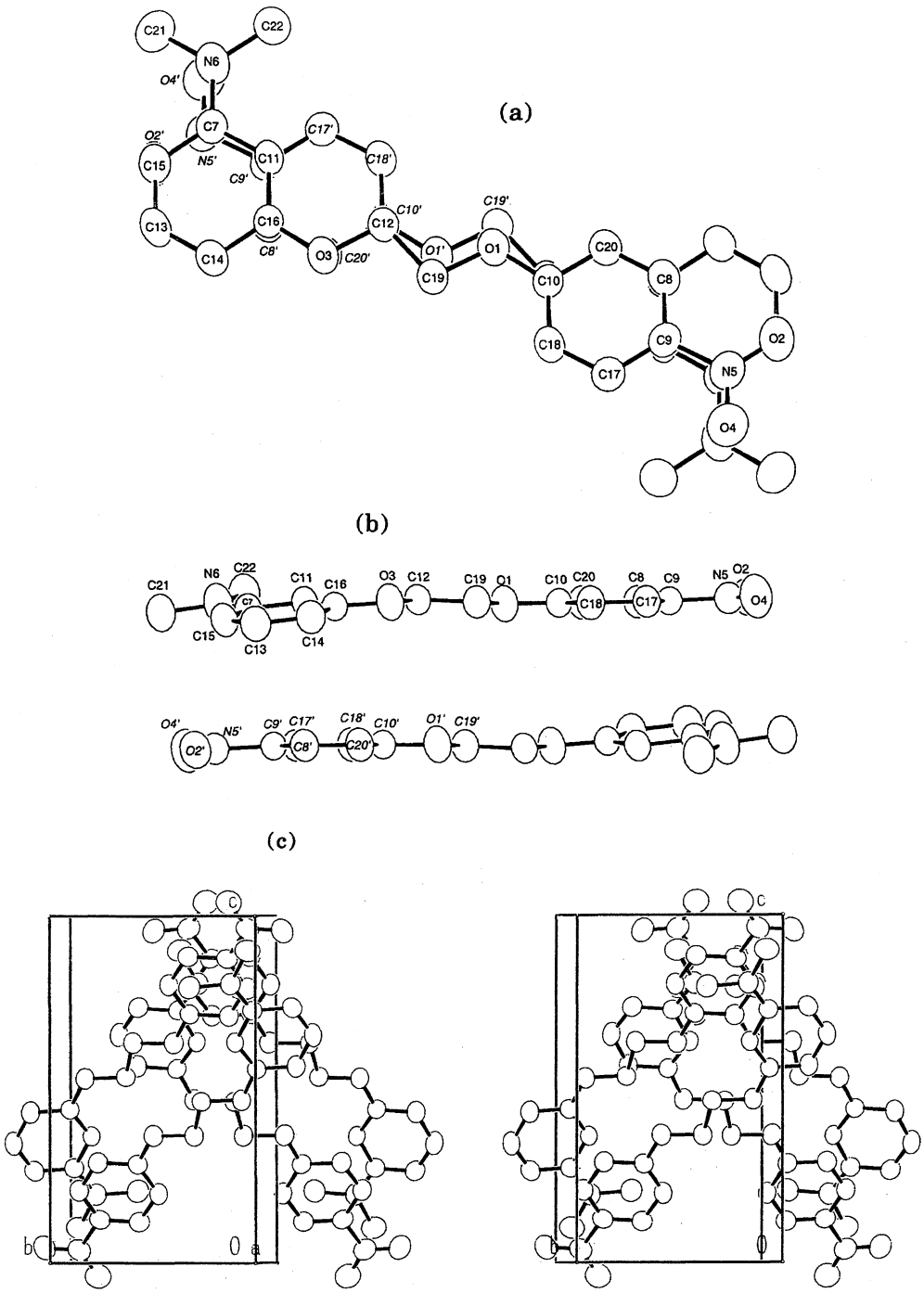

Fig. 1. (a) Projection of a molecular pair in a crystal of **1** along the line through C_{15} and $O_{2'}$ atoms, (b) side view of the molecular pair, and (c) stereoview of the unit cell.

that the molecular arrangement in the crystal of **1** is determined by a subtle balance of several intermolecular forces. CT interaction therefore is not so much stronger force than the other intermolecular forces as to be able to determine the crystal structure.

A similar type of CT interaction has been observed for *N*-methyl-*N*-[2-(*p*-nitrophenyl)ethyl]toluidine (**6**). In this case again, the phenomenon is restricted only to this homologue. Neither the higher homologues nor analogues (for instance, *N*-[2-(*p*-nitrophenyl)ethyl]- and *N*-[3-(*p*-nitrophenyl)propyl]anilines (**7** and **8**), and their *N*-methyl derivatives), exhibit spectral characteristics of the interaction in solid state,[13] though all these compounds in solution show an extra absorption due to *intramolecular* CT interaction[14,15] In the orange red crystal of **6**, a different arrangement of molecules is observed; the two aromatic rings in a molecule lie in two separate but almost parallel planes, with each donor-ring sandwiched between the two acceptor-rings of the other molecules and vice versa. It is also noticeable

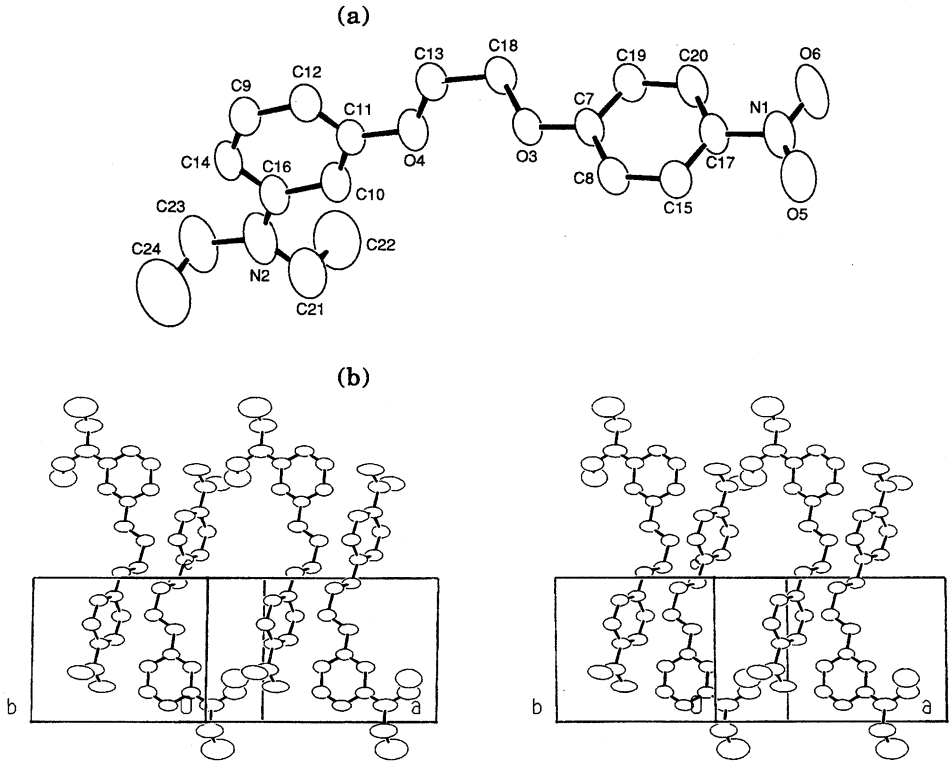

Fig. 2. (a) ORTEP drawing of a single molecule in a crystal of **2**, and (b) stereoview of the unit cell.

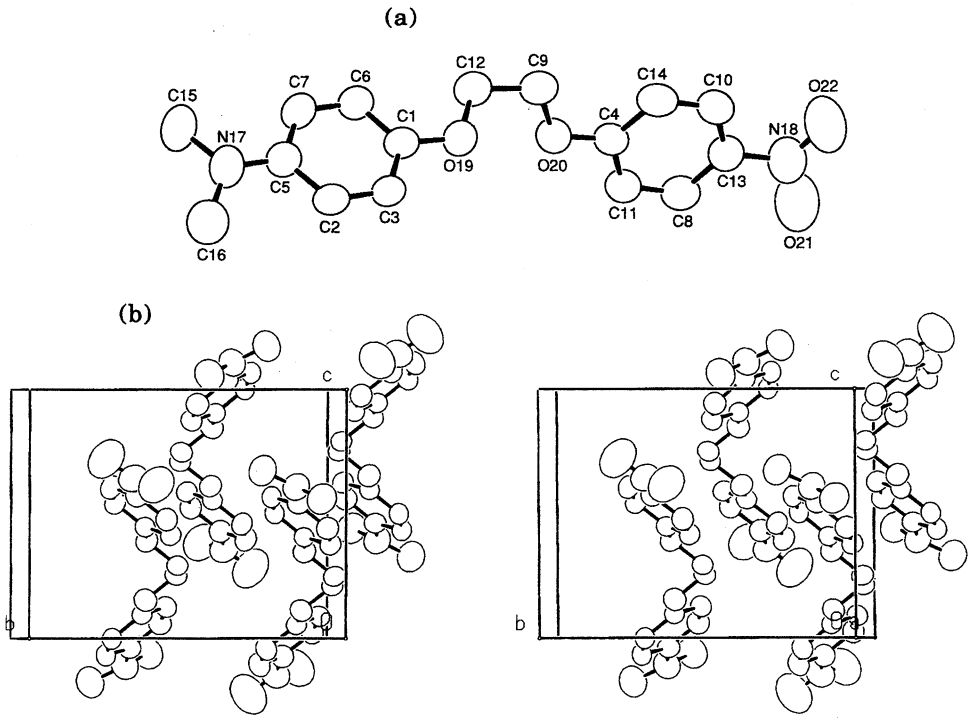

Fig. 3. (a) ORTEP drawing of a single molecule in a crystal of **3**, and (b) stereoview of the unit cell.

that the mean distance between the plane is 0.34 nm, sufficient for π–π overlap, but the overlap area of the aromatic rings is again very small. The role of CT interaction in the crystal of **6** seem to be similar to that in **1**.

Conformational Preference of O–C–C–O (or –N) Chain.[16] Comparison of the conformations of the single molecules illustrated in Figs. 1, 2, 3, and 4, shows that the dihedral angle of the chain O–C–C–O is 175.8° in **1**, 72.1° in **2**, and 72.7° in **3**, and that of O–C–C–N in **4** is 64°. In other words, except the *trans* rotamer with regard to C–C bond in **1**, *gauche* rotamer

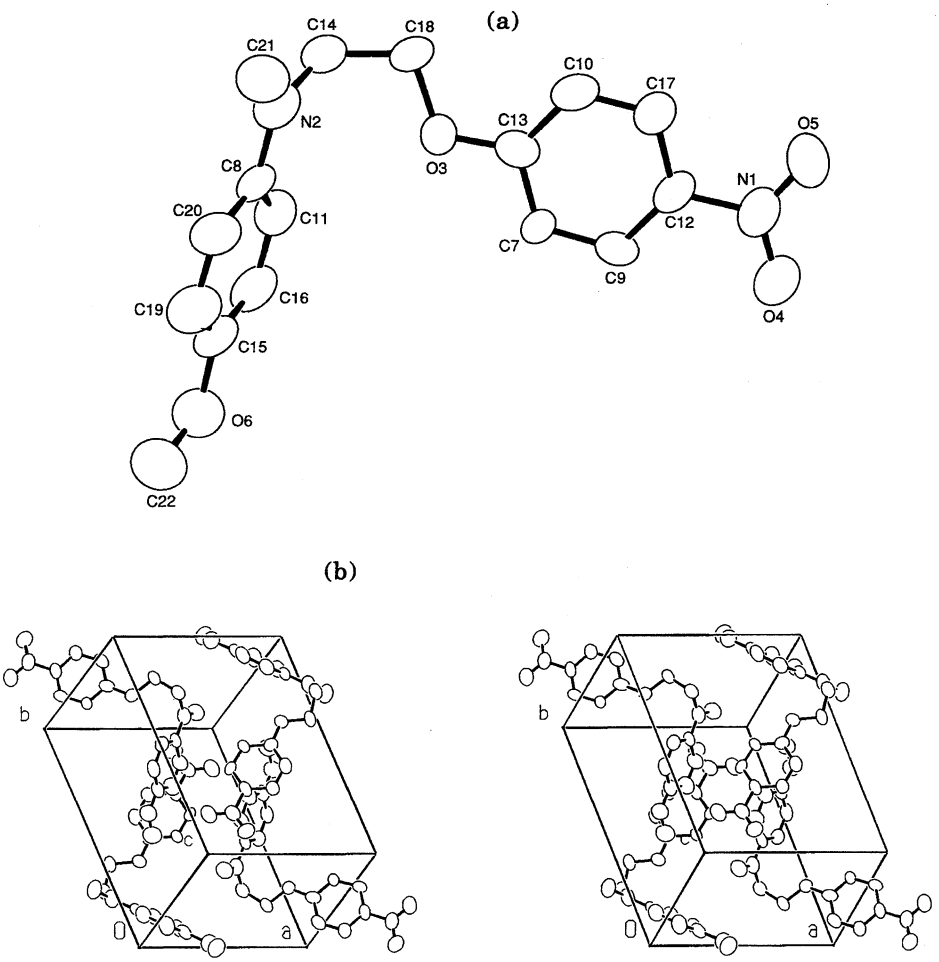

Fig. 4. (a) ORTEP drawing of a single molecule in a crystal of **4**, and (b) stereoview of the unit cell.

is the favorable conformation in the other compounds. 1,2-Diphenoxyethane[17] and its 4,4′-dichloro derivative have also been reported to be in *gauche* conformation in solid state.[18] A more detailed study using Raman and infrared spectroscopies has been reported by Ogawa et al. for the rotational isomers of 1,2-dimethyoxyethane, MeO–CH_2–CH_2–OMe, the simplest model for the study of the conformation of O–C–C–O bond.[19] They have found that the *gauche* rotamer predominates in liquid and crystalline states where intermolecular polar interaction is important.

In order to ascertain whether the predominance of the *gauche* rotamer is inherent in the structure or due to intermolecular forces in crystalline state, we estimated

Table 3. Comparison of Energy States Estimated for *gauche* and *trans* Conformers in 1,2-Diphenoxyethane and Its Derivatives

1-(R-phenoxy)-2-(R′-phenoxy)-ethane	Steric energy (MM2) (kJ mol^{-1})		Conformer energy difference (ΔE) (*gauche–trans*)	Heat of formation (PM3) (kJ mol^{-1})		Conformer energy difference (ΔE) (*gauche–trans*)
R and R′	*gauche*	*trance*	kJ mol^{-1}	*gauche*	*trance*	kJ mol^{-1}
R=H, R′=H	26.38	26.01	0.37	−78.14	−78.48	0.34
R=3-Me_2N– R′=4′-O_2N– (**1**)	59.67	60.28	−0.61	−141.79	−134.71	−7.08
R=4-Me_2N– R′=4′-O_2N– (**3**)	64.56	65.63	−1.07	−133.02	−132.42	−0.60

the energy difference between the *trans* and *gauche* rotamers for 1,2-diphenoxyethane, its 3-(dimethylamino)-4′-nitro and 4-(dimethylamino)-4′-nitro derivatives with the MM2 and PM3 calculations. The results are summarized in Table 3. It should be noted that the data are for the conformations of a single molecule free of all intermolecular interactions. For 1,2-diphenoxyethane, both methods suggest the *trans* rotamer is more favorable than the *gauche* by 0.34 (PM3) and 0.37 kJ mol^{-1} (MM2). The coincidence of the values is probably casual but the smallness of the difference is noticeable. For 1,2-dimethyoxyethane, the corresponding energy difference is estimated to be 0.42—0.59 kJ mol^{-1} by molecular dynamics simulations and ab initio calculations.[19,20] The results are not so much different from the values obtained for diphenoxy analogue. These data suggest that the hydrocarbon group attached to the ether oxygen is almost ineffective for the energy difference of the conformations. In these compounds therefore the energy is sufficiently small to be readily canceled or overcome by intermolecular forces, and polar *gauche* conformations are observed in solid state. For the compounds **1** and **3**, the results in Table 3 show that the *gauche* rotamers are favored by 0.6—1.1 (MM2) and 0.6—7.1 kJ mol^{-1} (PM3). Interestingly a large difference favoring the *gauche* rotamer was obtained by the PM3 approximation for **1**, though the observed conformation is *trans*. The change of the favorable rotamer for **1** and **3** from *trans* to *gauche* in the PM3 approximation may be due to the implicit involvement of electronic through-space interaction between the substituted aromatic rings, but the same tendency was also obtained by the MM2 calculation. Even admitting the ambiguity inherent in the theoretical approximations, we find that the agreement observed in these quite different methodologies is interesting. Anyway, considering that intermolecular interaction in solid state generally favors polar conformations, we think that the predominance of the *gauche* rotamer observed in the crystals of **2**, **3**, and **4** is not so surprising. Therefore, it may not be impertinent to state that a small energy difference between *gauche* and *trans* rotamers is characteristic for O–C–C–O bond and we can expect for this type of molecule in solid state to be in *gauche* conformation rather than *trans*.

In connection with the role of CT interaction force, the observed conformation of **1** can be interpreted to suggest that the intermolecular forces, with CT interaction and concomitantly induced forces added, is large enough to overcome the small energy difference and make the *trans* rotamer favorable over the *gauche*.

Conclusion. Only two compounds, **1** and **6**, among the tens of homologues and analogues of *N*-[(*p*-nitrophenyl)alkyl] and *N*-[(*p*-nitrophenoxy)alkyl] derivatives of arylamines[14,15,21] exhibited CT absorption in solid state so far. Thus the CT interaction possible in these weak donor–acceptor combinations can scarcely be the main intermolecular force to govern a molecular arrangement in a crystal. Probably it was fortuitous therefore for us to have encountered these compounds.

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