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Molecular and Crystal Engineering Studies of Two 2,4-Dinitroalkoxystilbenes: An Endeavor To Generate Efficient SHG Crystal[1]

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The crystal structure analyses of 2,4-dinitro-3′,4′-methylenedioxystilbene and 2,4-dinitro-3′,4′,5′-trimethoxystilbene have been carried out. Even though both the structures consist of molecular layers, the former crystallizes in a centrosymmetric space group, and the latter adopts a noncentrosymmetric structure. Rationale for the formation of these layers and their subsequent difference in stacking is presented in terms of the C–H···O interactions and nonplanarity of the molecular structure. The semiempirical calculations indicated that the hyperpolarizability varies a little (<3%) for a 20° rotation in the stilbene backbone. Due to a nonoptimal alignment of dipole in crystal, the dinitrotrimethoxystilbene is feebly SHG active in the powder state (0.2 × urea). Packing energy calculations and analyses of the X-ray powder patterns suggested the possible existence of another form of the dinitromethylenedioxystilbene. Crystal packing analyses of methylenedioxy, trimethoxy, and nitro groups reveal the importance of orientational effects and molecular nonplanarity in the generation of noncentrosymmetric crystal packing.

Introduction

Noncentrosymmetric crystals with large hyperpolarizabilities find varied applications in the field of nonlinear optics.[3] The use of chiral handles, incorporation of functional groups that encourage asymmetric intermolecular hydrogen-bonding, molecules possessing vanishing ground-state dipole moment and variation of counterion with ionic chromophores have been well-studied in generating noncentrosymmetric crystal structures.[4–7] In her work on nitroanilines and their molecular complexes, Etter was able to induce noncentrosymmetry by way of acentric hydrogen bonding.[8] Using the Cambridge Structural Database (CSD), she also attempted to recognize some molecular patterns which can assist in generating noncentrosymmetric structures.[9] In addition, it has been observed that the crystal structures of meta-substituted or less symmetric compounds are more likely to be noncentrosymmetric than other organic compounds.[3,10] Although there have been many such efforts to predict crystal structuers, routinely generating a highly polarizable noncentrosymmetric crystal is still an enigma.[11] It has been observed that heteroatom substituted planar aromatic compounds tend to form molecular layers/ribbons optimizing weak yet directional specific interactions. These layers stack at van der Waal separation optimizing a large number of C···C ($\pi\cdots\pi$) interactions.[12] A large hyperpolarizability β, is associated with strong electron-withdrawing and -donating groups on either end of a planar molecule, but in general, such a molecule tends to stack in a centrosymmetric structure optimizing the dipole–dipole interactions in addition to the van der Waal interactions.[13–15]

Recently an attempt has been made to crystallize an azo dye into noncentrosymmetric space group using some well-defined weak intermolecular forces and molecular nonplanarity.[16] Following a similar strategy, an effort is made here to crystallize a slightly nonplanar and highly polarizable substituted stilbene into a noncentrosymmetric structure. One of the possible ways to induce the nonplanarity in a stilbene *backbone* is to substitute a nitro group in an ortho position. Further, the *o*-nitro group can also act as an electron-withdrawing group. Thus the molecular and crystal structural studies on the two dinitroalkoxystilbenes are reported here. Packing potential energy calculations are used to recognize the possible polymorphic modifications and to evaluate the energy contributions by the individual groups in different nitroaromatic crystal structures. Since this work is in accord with many ideas of Etter, it is therefore appropriate that it appears among a series of papers to commemorate her.

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(3) For a review see: (a) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690. (b) *Non-linear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: Orlando, FL, 1987; Vols. 1 and 2. (c) *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Prasad, P. N., Williams, D. J., Eds.; John Wiley & Sons: New York, 1991. (d) *Crystal Engineering. The Design of Organic Solids*; Desiraju, G. R., Ed.; Elsevier: Amsterdam, 1989. (e) *Organic Materials for Non-linear Optics*; Special Publication No. 69; Hann, R. A., Blorr, D., Eds.; Royal Society of Chemistry: London, 1989.

(4) Zyss, J.; Nicoud, J. F.; Koquillay, M. J. *J. Chem. Phys.* **1984**, *81*, 4160.

(5) Tweig, R. W.; Jain, K. In *Nonlinear Optical Properties of Organic and Polymeric Materials*; ACS Symp. Ser. No. 233; Williams, D. J., Ed.; American Chemical Society: Washington, DC, 1983; p 57.

(6) Zyss, J. S.; Chemla, D. S.; Nicoud, J. F. *J. Chem. Phys.* **1981**, *74*, 4800.

(7) Marder, S. R.; Perry, J. W.; Schaefer, W. P. *Science* **1989**, *245*, 626.

(8) Etter, M. C.; Frankenbach, M. G. *Chem. Mater.* **1989**, *1*, 10.

(9) Etter, M. C.; Huang, K. *Chem. Mater.* **1992**, *4*, 824.

(10) Curtin, D. Y.; Paul, I. C. *Chem. Rev.* **1981**, *81*, 525.

(11) Gavezzotti, A. *J. Am. Chem. Soc.* **1991**, *113*, 4622.

(12) Sarma, J. A. R. P.; Desiraju, G. R. *Acc. Chem. Res.* **1986**, *19*, 222.

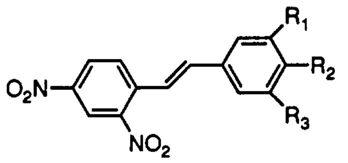
(13) Reference 3b, Vol. 1, p 130.

(14) Desiraju, G. R.; Krishna, T. S. R.; Sarma, J. A. R. P. *Chem. Phys. Letters* **1986**, *131*, 124.

(15) Gavezzotti, A. *J. Phys. Chem.* **1990**, *94*, 4319.

(16) Sarma, J. A. R. P.; Dhurjati, M. S. K.; Bhanuprakash, K.; Ravikumar, K. *J. Chem. Soc., Chem. Commun.* **1993**, 440.

0897-4756/94/2806-1369$04.50/0



2,4-dinitro-3′,4′-methylenedioxy-(*E*)-stilbene, DNMD, **1**: R_2 and R_3 = OCH_2O
2,4-dinitro-3′,4′,5′-trimethoxy-(*E*)-stilbene, DNTM, **2**: R_1 = R_2 = R_3 = OCH_3

Experimental Section

Preparation of Dinitroalkoxystilbenes. Compounds 1 and 2 were prepared by the condensation of the corresponding benzaldehydes with 2,4-dinitrotoluene.[17] Alkoxybenzaldehyde (24 mmol) and 2,4-dinitrotoluene (12 mmol) were refluxed in dry toluene (30 mL) and piperidine (6 mL) for 8 h. On powder samples of these stilbenes, SHG efficiencies were measured using the fundamental frequency (1064 nm) from a Nd:YAG laser following the Kurtz method.[18]

DNMD, 1. Red cubes of 1 were obtained from methanol solution by slow evaporation of the solvent, mp 148 °C; spectral analysis: UV (methanol) λ_{max} 394.7 nm, ϵ 13 680 ($\pi\pi^*$); IR (KBr) 3050, 1610, 1595, 1520, 1500, 1440, 1340, 1320, 1260, 960 cm^{-1}; δ ($CDCl_3$) 8.9 (d, 1H, 2 Hz), 8.35 (dd, 1H, 10 Hz), 8.05 (d, 1H, 10 Hz), 7.35 (d, 1H, 14 Hz), 7.3 (s, 1H), 7.15 (s, 1H), 7.1 (d, 1H, 4 Hz), 6.9 (d, 1H, 14 Hz), 6.1 (s, 2H); *m/e* 314 $(M)^{\bullet +}$, 297 $(M - OH)^+$, 268 $(M - NO_2)^+$, 180 $(M - C_8H_6O_2)^+$, 150 $(180 - NO)^+$, 135 $(M - C_7H_3N_2O_4)^+$.

DNTM, 2. The stilbene 2 was also recrystallized from methanol to yield red long thick needles; mp 189 °C; UV (methanol) λ_{max} 383.1 nm, ϵ 17 040 ($\pi\pi^*$); IR (nujol) 3025, 1600, 1580, 1530, 1510, 1500, 1460, 1340, 1320, 1240, 1260, 965 cm^{-1}; δ ($CDCl_3$) 8.85 (d, 1H, 2.5 Hz), 8.42 (dd, 1H, 10 Hz), 7.95 (d, 1H, 10 Hz), 7.55 (d, 1H, 18 Hz), 7.22 (d, 1H, 18 Hz), 6.78 (s, 2H), 3.88 (s, 3H), 3.9 (s, 3H), 3.93 (s, 3H); *m/e* 360 $(M)^{\bullet +}$, 345 $(M - CH_3)^+$, 329 $(M - OCH_3)^+$, 196 $(M - C_7H_4N_2O_3)^+$, 181 $(M - C_7H_3N_2O_4)^+$.

Crystal Structure Analyses of 1 and 2. The necessary crystallographic information of 1 and 2 is given in Table 1. The unit cell dimensions were determined by indexing 15 well-centered reflections with $25 \leq 2\theta \leq 40°$ on a Siemens R3m/v diffractometer. The crystal structures of 1 and 2 were solved by direct methods using the programs MULTAN80 and SHELX86, respectively.[19,20] Full-matrix least-squares refinement of positions and thermal parameters of all atoms was carried out using the program SHELX76.[21] The positional and equivalent atomic displacement parameters of 1 and 2 are given in Tables 2 and 3, respectively. Some of the dihedral angles and intramolecular H···O distances are given in Table 4. Various intermolecular C–H···O interactions are given in Table 5. Figures 1 and 2 are the ORTEP diagrams of 1 and 2, respectively, depicting the atomic displacement ellipsoids and atom numbering scheme.[22] The anisotropic atomic displacement parameters, bond lengths, bond angles, torsion angles, and structure factors for both the structures are given in the supplementary material (see paragraph at end of paper).

Computational Methodology. Complete geometrical optimizations of stilbenes 1 and 2 were carried out using the program MOPAC with the AM1 Hamiltonian.[23,24] The starting geometries used for these calculations are based on the X-ray structures. First-order hyperpolarizability β_0 was calculated by the finite field method (Table 6).[25] Packing potential energies (PPE) of 1, 2, and some other alkoxynitroaromatic compounds were calculated using the programs OPEC and PCK83 adopting Mirsky potentials; the results are given in Table 7.[26-28] The positions of hydrogens that were relocated at a C–H distance of 1.08 Å were used in the energy calculations. Partial atomic charges obtained from MOPAC were used to calculate the electrostatic contributions in the PPE. The calculated X-ray powder patterns were obtained using the program LAZY.[29]

Table 1. Crystallographic Information of DNMD, 1, and DNTM, 2[a,b]

	DNMD, 1	DNTM, 2
mol formula	$C_{15}H_{10}N_2O_6$	$C_{17}H_{16}N_2O_7$
mol wt	314	360
crystal system	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_12_12_1$
a (Å)	13.203 (2)	7.345 (1)
b (Å)	15.734 (2)	13.425 (2)
c (Å)	14.276 (2)	16.956 (2)
β (deg)	112.06 (1)	
υ ($Å^3$)	2748.5	1672.0
Z	8	4
d_{cal} (g cm^{-3})	1.52	1.43
d_{obs} (g cm^{-3})	1.49	1.42
F(000)	1296	752
μ (cm^{-1})	0.76	0.71
crystal size (mm^3)	0.20 × 0.17 × 0.15	0.25 × 0.20 × 0.19
T (K)	298	298
X-radiation (λ = 0.710 69 Å)	Mo Kα	Mo Kα
2θ range (deg)	$3 \rightarrow 50$	$3 \rightarrow 50$
$-h, h; -k, k; -l, l$	0,14; 0,16; −14,14	0,7; 0,14; 0,18
no. of obsd reflns	3159[a]	1292
no. of reflns with I_{obs}	2222 [$>2\sigma(I)$]	1026 [$>1.5\sigma(I)$]
no. of parameters	497	299
R	0.047	0.039
R_w	0.048	0.043
w (k, g)[b]	1.1992, 0.032 74	0.6627, 0.049 72
max Δ/σ	0.018	0.22
max and min $\Delta\rho$ (e $Å^{-3}$)	0.23, −0.19	0.15, −0.20

[a] Total number of reflections measured 3973 of which 3618 are unique. R_{int} = 0.043. [b] The above *k* and *g* values are used in the weighting function; $w = k/[\sigma^2(F_o) + (gF_o)^2]$.

Results and Discussion

Molecular Structures of Stilbenes 1 and 2. The geometrical optimizations using MOPAC, produce similar nonplanar conformations for stilbenes 1 and 2 which are shown in Figure 3 (P and Q). The angles between the various planes are given in Table 4 (set I). Even though the geometrical optimizations converge in a number of different conformations, only the most stable geometry of each stilbene is considered.[30] Each of the stilbene conformation obtained on optimization could occur in the enantiomeric conformation. In both stilbenes, while the dinitro and alkoxy phenyl groups are nearly parallel to each other, they make considerable angles (angle ϕ) with the double bond. The short distance between H7 and O1 (Table 4) can be considered as an intramolecular C–H···O hydrogen bonding. While the *p*-nitro group is in-plane with the phenyl ring, the *o*-nitro group is rotated (angle θ) by ~12°.

Stilbene 1 crystallizes in a monoclinic space group, $P2_1/c$ (Z = 8) with two molecules (A and B) in the asymmetric

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[17] Tiemann, B. G.; Marder, S. R.; Perry, J. W. *Chem. Mater.* **1990**, *2*, 690.

[18] Kurtz, S. K.; Perry, T. T. *J. Appl. Phys.* **1968**, *39*, 3798.

[19] Germain, G.; Main, P.; Woolfson, M. M. *Acta. Crystallogr., Sect. A* **1971**, *27*, 368.

[20] Sheldrick, G. M. SHELX86, a Crystallographic Structure Solution Package; University of Gottingen: Gottingen, 1986.

[21] Sheldrick, G. M. SHELX76, a Crystallographic Structure Refinement Package; University of Gottingen: Gottingen, 1976.

[22] Johnson, C. K. ORTEP; Report No. ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

[23] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

[24] Locally modified version of program MOPAC 4.0.

[25] Kurtz, H. A.; Stewart, J. J. P.; Dieter, K. M. *J. Comput. Chem.* **1990**, *11*, 82.

[26] Gavezzotti, A. *J. Am. Chem. Soc.* **1983**, *105*, 5220.

[27] Williams, D. E. PCK83, a program for Calculation of Crystal Packing and Non bonded forces; University of Louisville: Louisville, KY, 1983.

[28] Mirsky, K. *Acta. Crystallogr., Sect. A* **1976**, *32*, 199.

[29] Yvon, K.; Jeitschko, W.; Parthe, E. *J. Appl. Crystallogr.* **1977**, *10*, 73.

[30] The energy difference between the most stable conformer and any other fully converged conformer is <0.5 kcal/mol.

Table 2. Atomic Coordinates and Equivalent Atomic Displacement Parameters[a] for DNMD, 1. Esd's Are Given in Parentheses to the Last Significant Figure

atom	*x/a*	*y/b*	*z/c*	$U_{eq}{}^a$
		Molecule A		
O1a	−0.0719(3)	0.5619(2)	0.2259(3)	0.069(2)
O2a	−0.2049(3)	0.5026(2)	0.1038(3)	0.035(2)
O3a	−0.1052(3)	0.1953(2)	0.1208(3)	0.061(2)
O4a	0.0292(3)	0.1660(2)	0.0751(3)	0.068(2)
O5a	0.1522(3)	0.9132(2)	0.1709(3)	0.073(2)
O6a	0.3138(3)	0.9400(2)	0.1471(2)	0.076(2)
N1a	−0.1083(3)	0.5094(2)	0.1581(3)	0.046(2)
N2a	−0.0254(3)	0.2163(2)	0.1012(3)	0.041(2)
C1a	0.0647(3)	0.4796(2)	0.1297(3)	0.028(2)
C2a	−0.0316(3)	0.4495(2)	0.1393(3)	0.034(2)
C3a	−0.0625(3)	0.3651(3)	0.1303(3)	0.030(2)
C4a	0.0051(3)	0.3068(2)	0.1109(3)	0.031(2)
C5a	0.0991(3)	0.3315(3)	0.0980(3)	0.038(3)
C6a	0.1280(3)	0.4162(3)	0.1076(3)	0.032(3)
C7a	0.0943(3)	0.5700(3)	0.1373(3)	0.037(3)
C8a	0.1841(4)	0.6010(3)	0.1301(3)	0.034(3)
C9a	0.2184(3)	0.6896(2)	0.1350(3)	0.033(2)
C10a	0.1561(3)	0.7575(3)	0.1513(3)	0.035(3)
C11a	0.1964(3)	0.8379(2)	0.1536(3)	0.048(3)
C12a	0.2930(3)	0.8544(3)	0.1395(3)	0.052(3)
C13a	0.3558(4)	0.7906(3)	0.1250(3)	0.042(3)
C14a	0.3168(3)	0.7081(3)	0.1233(3)	0.040(3)
C15a	0.2227(5)	0.9796(3)	0.1602(5)	0.090(4)
H3a	−0.127(3)	0.353(2)	0.139(3)	0.04(1)
H5a	0.143(3)	0.293(2)	0.083(3)	0.04(1)
H6a	0.193(4)	0.435(3)	0.099(3)	0.07(1)
H7a	0.045(3)	0.607(2)	0.148(3)	0.04(1)
H8a	0.228(3)	0.567(3)	0.122(3)	0.05(1)
H10a	0.090(3)	0.745(2)	0.162(3)	0.05(1)
H13a	0.420(3)	0.802(2)	0.118(3)	0.04(1)
H14a	0.351(3)	0.664(2)	0.113(3)	0.05(1)
H15a1	0.243(4)	1.018(3)	0.222(4)	0.08(2)
H15a2	0.179(4)	1.011(3)	0.095(4)	0.09(2)
		Molecule B		
O1b	−0.5746(3)	0.1128(2)	0.2114(3)	0.065(2)
O2b	−0.7102(2)	0.1881(2)	0.1152(2)	0.033(2)
O3b	−0.6010(3)	0.4861(2)	0.1258(3)	0.056(2)
O4b	−0.4506(3)	0.5167(2)	0.1069(2)	0.068(2)
O5b	−0.3559(3)	−0.2345(2)	0.1504(3)	0.066(2)
O6b	−0.1905(3)	−0.2602(2)	0.1327(3)	0.082(2)
N1b	−0.6127(3)	0.1722(2)	0.1532(3)	0.040(2)
N2b	−0.5161(3)	0.4656(2)	0.1159(3)	0.045(2)
C1b	−0.4441(3)	0.2001(2)	0.1167(3)	0.030(2)
C2b	−0.5370(3)	0.2309(2)	0.1312(3)	0.029(2)
C3b	−0.5625(3)	0.3164(2)	0.1306(3)	0.034(2)
C4b	−0.4918(3)	0.3745(2)	0.1154(3)	0.036(2)
C5b	−0.3991(3)	0.3484(3)	0.0984(3)	0.043(3)
C6b	−0.3765(4)	0.2629(3)	0.0995(3)	0.041(3)
C7b	−0.4175(4)	0.1092(3)	0.1164(3)	0.043(3)
C8b	−0.3251(4)	0.0784(3)	0.1123(3)	0.047(3)
C9b	−0.2920(3)	−0.0104(3)	0.1153(3)	0.039(3)
C10b	−0.3532(4)	−0.0785(3)	0.1302(3)	0.035(3)
C11b	−0.3109(3)	−0.1591(3)	0.1354(3)	0.046(3)
C12b	−0.2123(4)	−0.1739(3)	0.1256(3)	0.053(3)
C13b	−0.1498(4)	−0.1096(3)	0.1113(3)	0.045(3)
C14b	−0.1913(4)	−0.0271(3)	0.1077(3)	0.046(3)
C15b	−0.2790(5)	−0.2999(3)	0.1516(5)	0.071(4)
H3b	−0.627(3)	0.335(3)	0.146(3)	0.07(1)
H5b	−0.354(3)	0.389(2)	0.089(2)	0.03(1)
H6b	−0.313(4)	0.248(3)	0.088(3)	0.08(2)
H7b	−0.477(4)	0.072(3)	0.122(3)	0.08(2)
H8b	−0.272(4)	0.119(3)	0.103(3)	0.07(1)
H10b	−0.420(3)	−0.072(2)	0.140(3)	0.05(1)
H13b	−0.083(4)	−0.118(3)	0.099(3)	0.06(1)
H14b	−0.154(3)	0.020(3)	0.095(3)	0.06(1)
H15b1	−0.248(3)	−0.321(3)	0.224(4)	0.07(2)
H15b2	−0.314(4)	−0.336(4)	0.097(4)	0.11(2)

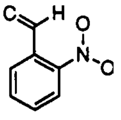
[a] $U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$. $\sigma(U_{eq}) = [\sigma^2 U_{11}(U_{22}U_{33})^{1/3}({}^1/_3 U_{11}{}^{-2/3}) + \sigma^2 U_{22}(U_{33}U_{11})^{1/3}({}^1/_3 U_{22}{}^{-2/3}) + \sigma^2 U_{33}(U_{11}U_{22})^{1/3}({}^1/_3 U_{33}{}^{-2/3})]^{1/2}$.

Table 3. Atomic Coordinates and Equivalent Atomic Displacement Parameters[a] of DNTM, 2. Esd's Are Given in Parentheses to the Last Significant Figure

atom	*x/a*	*y/b*	*z/c*	$U_{eq}{}^a$
O1	0.5912(8)	0.0249(3)	1.0163(2)	0.145(5)
O2	0.663(1)	−0.0913(3)	0.9391(3)	0.230(7)
O3	0.6068(6)	−0.0540(3)	0.6615(2)	0.087(3)
O4	0.5730(8)	0.0923(4)	0.6115(2)	0.132(5)
O5	0.6706(7)	0.6357(2)	1.1223(2)	0.105(3)
O6	0.7075(5)	0.5464(3)	1.2607(2)	0.070(3)
O7	0.7079(6)	0.3463(3)	1.2740(2)	0.083(3)
N1	0.6327(8)	−0.0048(3)	0.9517(2)	0.075(3)
N2	0.6005(7)	0.0370(4)	0.6675(2)	0.070(4)
C1	0.6605(7)	0.1693(4)	0.8953(3)	0.040(3)
C2	0.6447(7)	0.0656(3)	0.8849(2)	0.042(3)
C3	0.6276(9)	0.0230(4)	0.8111(3)	0.055(4)
C4	0.6267(8)	0.0826(3)	0.7457(3)	0.047(3)
C5	0.6489(9)	0.1843(4)	0.7515(3)	0.056(4)
C6	0.6663(9)	0.2261(4)	0.8253(3)	0.064(4)
C7	0.6736(8)	0.2197(4)	0.9736(3)	0.045(4)
C8	0.6350(8)	0.3155(4)	0.9837(3)	0.051(3)
C9	0.6496(8)	0.3718(3)	1.0582(3)	0.043(3)
C10	0.6463(9)	0.4759(4)	1.0532(3)	0.053(4)
C11	0.6633(8)	0.5328(3)	1.1212(3)	0.058(4)
C12	0.6796(8)	0.4876(4)	1.1943(3)	0.051(4)
C13	0.6821(8)	0.3833(4)	1.1997(3)	0.047(4)
C14	0.6667(8)	0.3256(4)	1.1309(3)	0.047(3)
C15	0.658(2)	0.6862(5)	1.0478(4)	0.127(8)
C16	0.580(1)	0.5357(6)	1.3243(5)	0.071(6)
C17	0.698(2)	0.2417(6)	1.2848(5)	0.123(9)
H3	0.604(7)	−0.038(4)	0.806(3)	0.04(2)
H5	0.663(9)	0.220(4)	0.709(3)	0.07(2)
H6	0.667(7)	0.305(4)	0.829(3)	0.06(1)
H7	0.732(7)	0.185(3)	1.015(3)	0.03(1)
H8	0.577(6)	0.352(3)	0.940(2)	0.02(1)
H10	0.631(8)	0.502(4)	1.006(3)	0.05(1)
H14	0.653(8)	0.256(4)	1.139(3)	0.05(1)
H15A	0.68(1)	0.746(5)	1.066(4)	0.08(2)
H15B	0.52(1)	0.670(5)	1.031(4)	0.09(2)
H15C	0.755(9)	0.667(4)	1.011(4)	0.06(2)
H16A	0.57(1)	0.595(7)	1.357(5)	0.12(3)
H16B	0.59(1)	0.460(8)	1.346(6)	0.16(4)
H16C	0.48(1)	0.527(8)	1.306(5)	0.14(4)
H17A	0.74(1)	0.235(5)	1.340(4)	0.09(2)
H17B	0.566(9)	0.228(4)	1.284(3)	0.05(2)
H17C	0.71(1)	0.202(6)	1.247(4)	0.10(3)

[a] $U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$. $\sigma(U_{eq}) = [\sigma^2 U_{11}(U_{22}U_{33})^{1/3}({}^1/_3 U_{11}{}^{-2/3}) + \sigma^2 U_{22}(U_{33}U_{11})^{1/3}({}^1/_3 U_{22}{}^{-2/3}) + \sigma^2 U_{33}(U_{11}U_{22})^{1/3}({}^1/_3 U_{33}{}^{-2/3})]^{1/2}$.

unit. While molecule A is nearly planar (angle ϕ 3°), molecule B is slightly nonplanar (angle ϕ 6.9°). The *o*-nitro group adopts different orientations in these two molecules (angle θ 49° and −41° in A and B, respectively). The torsional freedom of this group is evident from these orientations which represent the two possible minima on the potential surface. In both the molecules, the *o*-nitro group is involved in the intramolecular C–H···O hydrogen bonding (Table 4) which may be helpful in "locking" the conformation of these molecules. Ignoring the subtle differences in the stilbene *backbone*, the two molecules are nearly enantiomeric (Figure 3) and may not be interconvertible at ambient temperatures. In comparison with 1, the ethylenic moiety in 2 makes a larger angle with the phenyl ring and the *o*-nitro group tends to be more nearly coplanar with the phenyl ring to which it is attached, as observed from angles θ and ϕ in Table 4. The molecule adopts a chiral conformation in the crystal.



fragment 1

The orientation of the *o*-nitro group with respect to an alkenyl group in nitroaromatic compounds is analyzed from

Table 4. Some of the Dihedral Angles (deg) and Intramolecular C–H···O (H7···O1) Distances (Å) in MOPAC-Optimized (Set I) and X-ray Structures (Set II) of Stilbenes 1 and 2 and Other Dinitrophenyl Compounds

plane I: C1 C2 C3 C4 C5 C6 [phenyl with nitro groups]
plane II: C9 C10 C11 C12 C13 C14 [phenyl with alkoxy groups]
plane III: C1 C7 C8 C9 [ethylene group]
plane IV: N1 O1 O2 [*o*-nitro group]
plane V: N2 O3 O4 [*p*-nitro group]

compound	I–III ϕ	II–III	I–II	I–IV θ	I–V	C–H···O dist
			Set I			
DNMD, **1**	–36	25	–11	–12.1	0.4	2.24
DNTM, **2**	–36	27	–9	–11.7	0.3	2.24
DNCA[a]	44			11.2	0.7	2.31
			Set II			
DNMD(A), **1**	–3.0	1.6	–3.2	48.8	–6.1	2.31
DNMD(B), **1**	–6.9	4.8	–4.6	–41.2	3.6	2.32
DNTM, **2**	–22.2	15.4	–6.8	–20.6	–11.4	2.26
DNCA[a]	38.0			23.6	15.3	2.43
34CP[a]	–2.1			–35.3	–4.3	2.18
25CP[a]	–3.8			–33.6 (33.6)[b]	–6.6	2.18

[a] 2,4-Dinitrophenyl group in DNCA: 2,4-dinitrocinnamic acid.[49] 34CP: 1:1 complex of 2,4-dinitrocinnamic acid and 3,4-dimethoxycinnamic acid.[50] 25CP: 1:1 complex of 2,4-dinitrocinnamic acid and 2,5-dimethoxycinnamic acid.[32] [b] The *o*-nitro group is disordered in two possible orientations.

Table 5. Geometrical Details of Intermolecular C–H···O Interactions.[a] C···O Distances Are Given in Parentheses

		H···O distance (Å)	C–H···O angle (deg)
	DNMD, **1** (in Figure 6)		
a	H5a–O2b ($1 + x, 1 + y, z$)	2.30 (3.31)	156.2
b	H8a–O3b ($1 + x, y, z$)	2.33 (3.37)	161.8
c	O3a–H8b (x, y, z)	2.35 (3.40)	162.8
d	O2a–H5b (x, y, z)	2.45 (3.50)	164.5
e	O3a–H6b (x, y, z)	2.59 (3.63)	161.0
f	H6a–O3b ($1 + x, y, z$)	2.60 (3.65)	164.3
g	H14a–O3b ($1 + x, y, z$)	2.70 (3.60)	146.5
h	H13a–O5a ($1 + x, 1 + y, z$)	2.72 (3.70)	151.1
	DNTM, **2** (in Figure 8a)		
a	O6–H6 ($1.5 - x, 1 - y, 0.5 + z$)	2.43 (3.37)	144.4
b	O2–H17A ($1.5 - x, - y, - 0.5 + z$)	2.52 (3.45)	143.8
c	O5–H5 ($1.5 - x, 1 - y, 0.5 + z$)	2.56 (3.51)	145.8
d	O3–H17B ($1.5 - x, - y, - 0.5 + z$)	2.62 (3.59)	148.7
	DNTM, **2** (in Figure 8b)		
e	O3–H8 ($1 - x, - 0.5 + y, 1.5 - z$)	2.47 (3.51)	162.2
f	O4–H15B ($1 - x, - 0.5 + y, 1.5 - z$)	2.57 (3.43)	136.7
g	O4–H10 ($1 - x, - 0.5 + y, 1.5 - z$)	2.58 (3.57)	152.4
h	O1–H16A ($1 - x, - 0.5 + y, 2.5 - z$)	2.58 (2.99)	102.0

[a] Entries in each category are arranged in increasing order of H···O distance.

the data retrieved from CSD using the fragment 1.[31] However, there are only eight hits. When the corresponding values obtained from **1**, **2**, 2,4-dinitrocinnamic acid, DNCA and its 1:1 complex with 2,5-dimethoxycinnamic acid, 25CP (Table 4) are also included in the analysis, the mean H···O distance is 2.38(16) Å (H···O minimum and maximum distances are 2.083 and 2.632 Å, respectively), and the other results are given in Figure 4.[32]

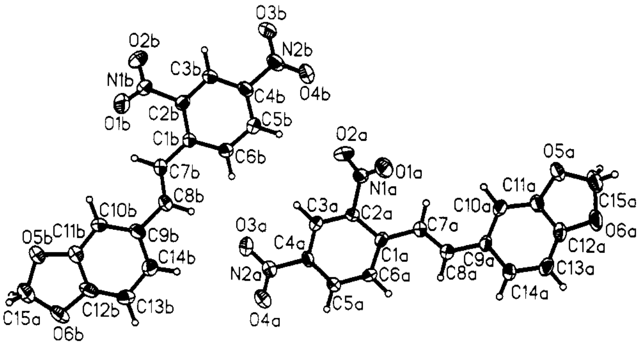


Figure 1. ORTEP plot of two symmetry independent molecules in DNMD, **1**, with 50% thermal ellipsoids and the atom numbering scheme.

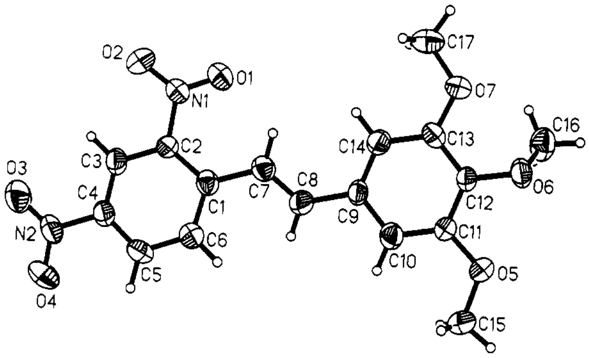


Figure 2. ORTEP plot of DNTM, **2**, with 50% thermal ellipsoids and the atom numbering scheme.

Table 6. Calculated Heat of Formation (H_f), Dipole Moment (μ), and First-Order Hyperpolarizability β_0[a] of Stilbenes 1 and 2[a,b]

compound	heat of formation (kcal/mol)	dipole moment (D)	β_0 ($\times 10^{-30}$ esu)
		Set I	
DNMD, 1	15.88	6.18	19.5
DNTM, 2	–33.40	4.36	16.2
		Set II	
DNMD(A), 1	17.19	6.29	18.3
DNMD(B), 1	16.23	6.25	19.5
DNTM, 2	–32.37	4.29	17.6

[a] β_0 is the hyperpolarizability at zero field calculated by employing a constant dc field. [b] While geometries of Set I molecules are obtained after complete geometrical optimization using MOPAC, the conformation of Set II molecules is that of X-ray structures with MOPAC optimised bond lengths and angles. The torsion angles of the non-hydrogen atoms in the completely optimised geometry were changed to the values of X-ray structure and H_f, μ and β_0 values are determined.

Angles θ and ϕ are inverse related, and this could be due to steric repulsion. These angles are well-distributed over a wide range (hence their esds are high) to suggest that in crystal, both inter- and intramolecular forces could decide the relative orientation of these groups.

The molecular properties like heat of formation (H_f), and β_0 are calculated for the completely optimized stilbenes and are given in Table 6 (set I). The conformation of these optimized stilbenes is changed to that of X-ray structures by changing the torsion angles and again these molecular properties are calculated (set II). The difference in the H_f between set I and II may reflect the necessary energy needed to change the preferred nonplanar conformation of a gaseous stilbene molecule to a conformation observed in the crystal. This energy is 1.31 (molecule A), 0.35 (molecule B) and 1.03 kcal/mole for stilbene **1** and **2**, respectively.

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(31) Statistical analyses were performed on the data retrieved from the CSD excluding the metal, transition-metal, error, polymer, duplicate and disorder containing structures with diffractometer data and having σ in C–C bond length <0.01. An upper limit of 0.1 in *R* factor was also considered to increase the accuracy of the analyses: Allen, F. H.; Bellard, S.; Brice, M. D.; Cartright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, B. G.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. G. *Acta. Crystallogr. Sect. B* **1979**, *35*, 2331.

(32) Sharma, C. V. K.; Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1991**, 1239.

Table 7. Packing Potential Energies (PPE, kcal/mol), Space Group, Number of Molecules in the Unit Cell Z, Packing Coefficient PC, and the Group Contributions to the PPE of Some Alkoxynitro Compounds

compound[a]	PPE[b]	sp gr	Z[c]	PC	group contribution	
					methylenedioxy	
MDCA	−88.9 (−7.3)	$P\bar{1}$	1_D	0.74	−9.11	
MDAC	−93.4 (−16.2)	$P\bar{1}$	1_D	0.73	−9.52	
MDCL	−86.5 (+2.8)	$P\bar{1}$	1_D	0.75	−9.59	
MDNS	−53.2 (−12.4)	$P2_1/c$	4	0.75	−9.28	
DNMD(A), 1	−69.2 (−11.5)	$P2_1/c$	8	0.72	−8.81	
DNMD(B), 1	−68.8 (−12.6)				−9.08	
DNMD1	−68.4 (−11.7)	$P2_1/n$	4	0.72	−8.93	
					trimethoxy	
TMAC	−93.2 (−5.3)	$P2_1/n$	2_D	0.74	−19.54	
DNTM, 2	−82.2 (−17.5)	$P2_12_12_1$	4	0.71	−19.06	
					nitro	
					ortho	para
DNCA	−97.2 (−19.0)	$P2_1/n$	2_D	0.71	−5.50	−6.58
34CP	−102.1 (−17.8)	$P\bar{1}$	2	0.73	−5.90	−6.11
25CP	−96.6 (−19.1)	$P\bar{1}$	2	0.70	−5.06[d]	−6.17
DNTM, 2					−5.86	−6.51
DNMD(A), 1					−5.81	−5.88
DNMD(B), 1					−5.85	−5.77
DNMD1					−6.15	−6.69

[a] MDCA: 3,4-methylenedioxycinnamic acid.[46] MDAC: 3,4-methylenedioxyphenylpropiolic acid.[41] MDCL: 6-chloro-3,4-methylenedioxycinnamic acid.[47] MDNS: 3,4-methylenedioxynitrostyrene.[48] DNMD1: stilbene 2 with $Z = 4$, $P2_1/n$. TMAC: 3,4,5-trimethoxyphenylpropiolic acid.[41] [b] The electrostatic contributions are given in parentheses. [c] In the case of acids, the O–H···O bonded dimer was considered as a single molecular entity. [d] The o-nitro group is disordered in two different orientations.

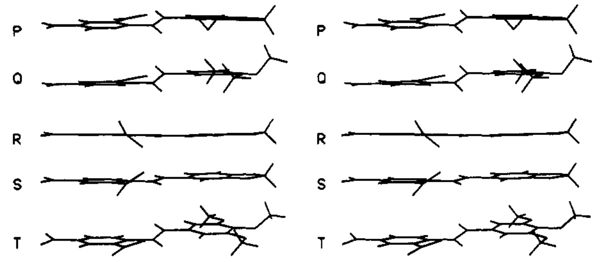
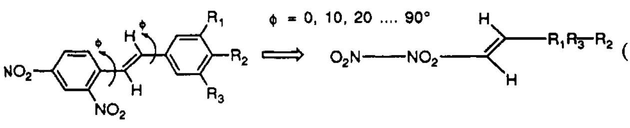


Figure 3. Stereodiagrams viewed nearly along the plane of the phenyl ring containing nitro groups of MOPAC optimized conformations of 1 (P) and 2 (Q), X-ray observed conformations of 1 molecule A (R) and B (S) and 2 (T).

Effect of Molecular Structure on Hyperpolarizability. The extent of nonplanarity in the stilbene molecule should effect the conjugation across the double bond vis-a-vis the hyperpolarizability, β. The variation in the H_f and β_0 is studied in 1 and 2 for an increase in angle ϕ. Initially, the torsion angles in an optimized stilbene are altered to generate a planar conformation. Subsequently, both the phenyl groups are rotated, such that they are always parallel to each other and make angles 0 to 90° in steps of 10° with the double bond (eq 1). These generated structures are further optimized keeping the angle ϕ unchanged. The results are given in Figure 5.



(1)

From these calculations, it has also been observed that angles ϕ and θ are highly correlated in both the stilbenes; as one decreases, the other increases, which is in agreement with the observation made earlier from the crystal structure data of nitroaromatic compounds (Figure 4). Figure 5 is the plot of the normalized differences in H_f as a function of angle ϕ. To adopt a planar conformation ~1.0 and ~1.2 kcal/mol are required by 1 and 2, respectively. As angle ϕ increases, the interaction between the electron-donating and -withdrawing groups through the double bond decreases, resulting in a decrease in β_0 (Figure 5). However, β_0 does not follow a linear relationship with the angle ϕ: initially it changes very little at small values of ϕ and falls off more rapidly at higher values of ϕ. In fact, it decreases by ≤3% for an initial 20° rotation in ϕ.

```
    4.0    13.0     22.0     31.0     40.0
    +I--------I--------I--------I--------I+——→ ANGLE θ
85.0-                                    -  ACROSS    DOWN
    I                                    I angle θ   angle ϕ
    I                                    I        MEAN:
    I         *                          I  23.837    40.635
65.0-  *                                 -        SDEV:
    I                 *    *             I   9.877    26.913
    I                                    I      MINIMUM:
    I                                    I   5.516     3.440
45.0-                                    -      MAXIMUM:
    I                  D *               I  35.900    71.993
    I                                    I
    I                                    I   8 POINTS PLOTTED
25.0-                C        *          -   0 POINTS OMITTED
    I                                    I
    I                                    I   CORREL. COEFF.
    I                                    I      -0.827
 5.0-                         *   F *    B
    I                              E     A
  ↓ +I--------I--------I--------I--------I+
ANGLE ϕ
```

Figure 4. Scatter plot showing the correlation between angles of the o-nitro group (angle θ) and the ethylenic group (angle ϕ) obtained from the data retrieved from CSD. A–F refer to (top to bottom) the molecules in set II of Table 4.

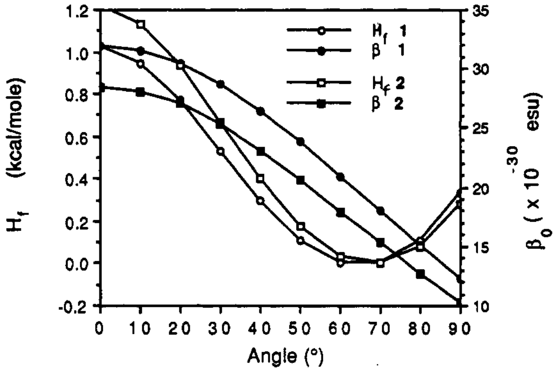


Figure 5. Variations of the normalized difference in heat of formation, ΔH_f, and hyperpolarizability, β_0, with angle ϕ in stilbenes 1 and 2.

Crystal Structure of Stilbene 1. The crystal structure of 1 is characterized by the stacking of molecular sheets parallel to (001). Successive sheets are inverse related and are separated by 3.28 Å. Each sheet is generated by the two symmetry-independent and their translation related molecules. One such molecular sheet is given in Figure 6. The molecular sheet is generated by a number of well-directed intermolecular C–H···O interactions (Table 5).[12,33] Within the sheet, every molecule A is surrounded by four molecules of B as well as two molecules of A and vice versa. Molecule B is pseudo related to molecule A either by a screw relation along a or by a glide relation perpendicular to b. The p-nitro group is involved in C–H···O contacts with the hydrogens of ethylenic and phenyl groups of a neighboring molecule (b, c, e, f, and g

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(33) Desiraju, G. R. Acc. Chem. Res. 1991, 24, 290.

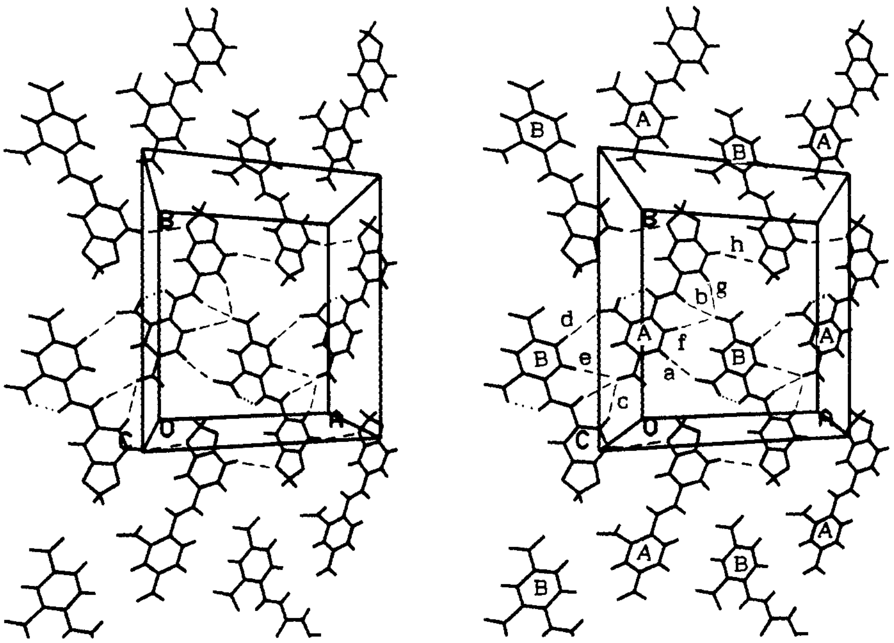

Figure 6. Stereoview of a molecular sheet parallel to (001) plane in the stilbene 1. While the intramolecular C–H···O interactions are marked with dotted lines, intermolecular C–H···O contacts (a–h) listed in Table 5 are shown with dashed lines.

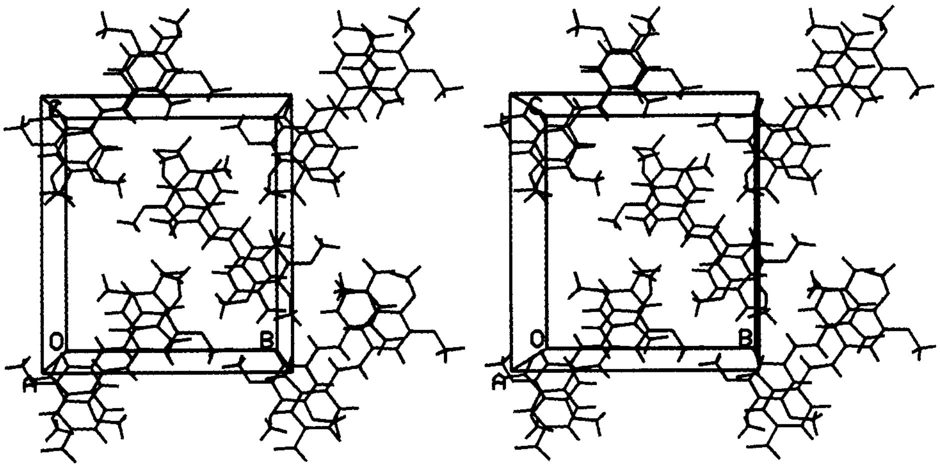

Figure 7. Stereodiagrams of the crystal structure of stilbene 2 viewed down the *a* axis.

in Figure 6 and Table 5). A "ziplike" arrangement of either dinitro or methylenedioxy phenyl groups along the [100] direction could be a consequence of the lateral C–H···O interactions adopted by these groups (a, b, c, d, e, f, and h in Figure 6 and Table 5).[34-37] These interactions may contribute the necessary amount of energy (~1.0 kcal/mol from Figure 5) to change the preferred nonplanar conformation (as calculated for the gas phase) into a planar conformation (as in crystal). Thus, the dilemma in optimizing the opposing inter and intramolecular forces may result the two molecules in the asymmetric unit. In spite of small conformational differences, both molecules A and B adhere to the formation of molecular sheets. These sheets are stacked in such a way that a phenyl ring with electron donating groups overlaps with another having electron withdrawing groups and vice versa. Such an arrangement may lead to the optimization of the charge-transfer (dipole–dipole) interactions in addition to the C···C ($\pi \cdots \pi$) interactions. The crystal structure of 1 is the result of a natural packing of a pseudoracemic mixture, i.e., centrosymmetric structure.

Crystal Structure of Stilbene 2. A corrugated sheet is commonly formed by the planar aromatic compounds crystallizing in the orthorhombic or monoclinic space groups.[12] The crystal structure of 2 is characterized by corrugated sheets. Successive sheets along [100] are screw related with the mean molecular plane nearly parallel (~2°) to (100). The crystal structure of 2, looking down the *a* axis is given in Figure 7. The corrugated sheets can be generated in either of the two possible ways as shown in Figure 8. In either of them, a molecule at the center is surrounded by the four screw (along *b* and *c*) and two translation related (along *b*) molecules. In spite of some subtle differences, the relative molecular orientation is similar to that of 1 (Figures 6 and 8a or 8b). The aromatic hydrogens are able to form the C–H···O interactions with the alkoxy oxygens of a neighbouring molecule (a and c in Figure 8a and Table 5). The *o*-nitro group is also

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(34) Desiraju, G. R. *Mol. Cryst. Liq. Cryst.* **1992**, *211*, 63.

(35) Sharma, C. V. K.; Pannerselvam, K.; Pilati, T.; Desiraju, G. R. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2209.

(36) Dhurjati, M. S. K.; Sarma, J. A. R. P.; Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1991**, 1702.

(37) *Hydrogen bonding in Biological Structures*; Jeffrey, G. A.; Saenger, W., Springer-Verlag: Berlin, 1991; pp 30, 156.

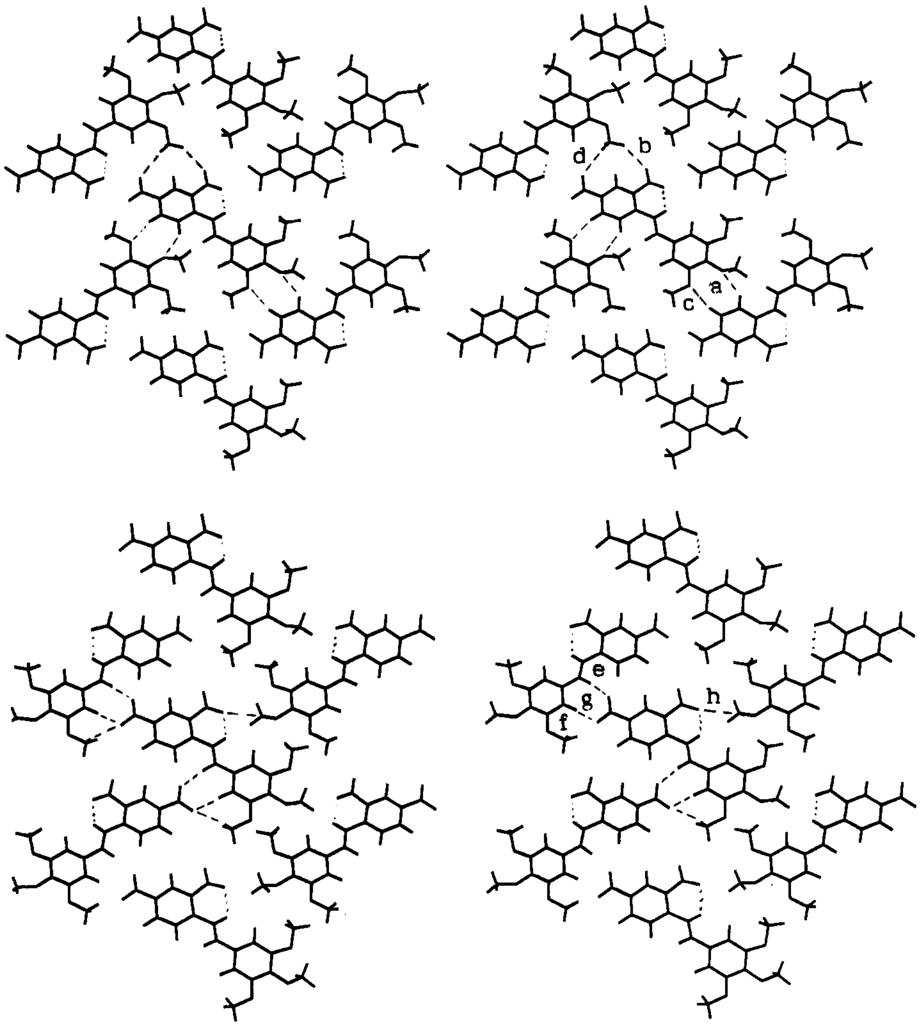

Figure 8. (a and b) Stereoplots of two possible corrugated molecular sheets in **2**. The C–H···O interactions (a–h) listed in Table 5 are marked and are shown with dashed lines in both sheets.

involved in the C–H···O interactions with one of the neighboring molecules (b in Figure 8a and Table 5). The *p*-nitro group forms the C–H···O contacts with the ethylenic and aromatic hydrogens of a neighboring screw related molecule (e, f, and g in Figure 8b and Table 5).[35] Since angle ϕ is ~22°, the *p*-nitro group also twists by ~11° to optimize these contacts. Because of the nonplanar conformation of **2**, the C–H···O interactions are both intra- and interlayered. Although the directional character of C–H···O interactions is maintained to some extent, these interactions are slightly weaker (greater H···O distances; Table 5) or at the best of equal strength in **2** compared to **1** (Table 5). Thus in **2**, the C–H···O interactions along the sheets, contribute the same if not less amount of energy (~1.0 kcal/mol as in **1**) to change a preferred highly nonplanar conformation (angle $\phi \sim 70°$ as calculated in the gas phase) to a less nonplanar conformation (angle $\phi \sim 20°$ in the crystal). In the crystal, the dipole of **1** aligns with *a*, *b*, and *c* axes by 101.3, 11.23, and 86.82°, respectively, and these values are far from the optimal value of 54.7° to show any significant SHG activity.[3b] When the powder SHG efficiencies are measured using a Nd:YAG laser, **1** is inactive, which is in accordance with its crystal structure, and **2** exhibits slight activity (~0.2 × urea).

Packing Potential Energy Calculations. Packing energies for stilbenes **1** and **2** and other related molecules listed in Table 7 have been calculated. The packing coefficient of methylenedioxy compounds is higher than that of trimethoxy compounds, and it could be due to the relatively stronger C–H···O interactions. The respective PPE contribution of methylenedioxy, trimethoxy, and nitro groups does not vary in different crystal structures indicating the similar nature of the interactions adopted by these groups (Table 7).

It is possible to consider the crystal structure of **1** in terms of a nonconventional space group $B2_1/c$ (unique axis *b* and $Z = 8$) with only a single set of equivalent molecules in the asymmetric unit because of the pseudo-glide/screw relation between molecules A and B. Employing the standard cell reduction procedures, a new cell of half the magnitude with $a = 7.69$, $b = 15.73$, $c = 11.39$ Å, $\beta = 94.82°$, space group $P2_1/n$, and $Z = 4$ is obtained (DNMD1).[38] In fact, the data transformed to the new cell contained a large number of strong and observed *hkl* reflections with $h + l = 2n + 1$ which should have been systematically absent.[39] The structure of stilbene **2** with respect to new cell (DNMD1) was generated on minimization of PPE with respect to the molecular rotations and translations. The positional parameters of this form are deposited as supplementary material. The PPE difference

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[38] *International Tables for Crystallography*; Ibers, J. A.; Hamilton, W. C.; Kynoch Press: Birmingham, 1974; Vol. 1, p 530.

[39] 13, 35, 233, and 341 reflections have intensities greater than 100σ, 50σ, 20σ, and 10σ respectively.

between the two forms of 2 is only ~1.2 kcal/mol (Table 7).

X-ray powder patterns of 1 and 2 were recorded. Also, these patterns were generated based on the observed $P2_1/c$ and the unobserved $P2_1/n$ structures of 1. The experimental pattern does not match with either of the individual calculated patterns, but it is in good agreement with the 1:1 combination of these two patterns (Figure 9). On the basis of these patterns and the small difference in PPE between the two forms (DNMD and DNMD1), it is believed that both the forms coexist at room temperature. On the other hand, the experimental and calculated powder patterns of 2 show a very good agreement, indicating that only one form exists at room temperature.

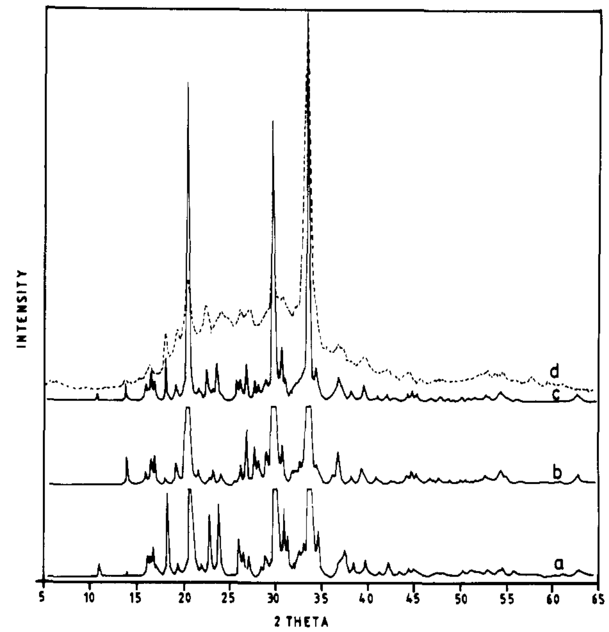
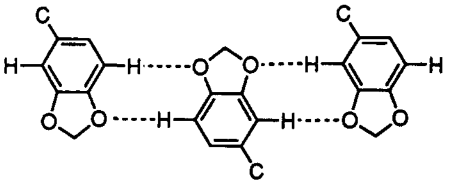


Figure 9. X-ray powder patterns of 1. (a) Pattern calculated based on the observed structure, $P2_1/c$. (b) Pattern calculated based on the unobserved structure, $P2_1/n$. (c) A 1:1 combination of the patterns a and b. (d) X-ray powder pattern recorded on the powder sample of 1.

Polymorphism is a common phenomenon in molecular solids and occurs frequently in substituted stilbenes.[40] Comparing the calculated and experimental X-ray powder patterns would help in identifying the other polymorphic forms. Because there is a need to obtain a noncentrosymmetric structure while designing an efficient SHG crystal, such an exercise should routinely be carried out in many cases.

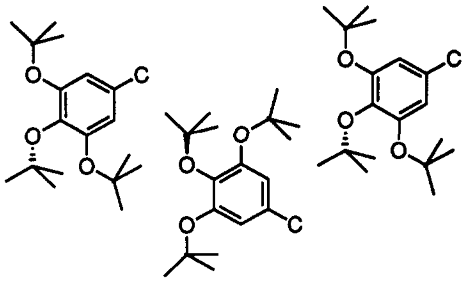
Crystal Engineering Studies of Alkoxy and Nitro Groups. The principles of crystal engineering can be used to determine the regularities of packing of certain kinds of molecules and substituents which can be used to obtain certain kinds of desired packing.[3d,12,16] The study of packing modes of methylenedioxy, trimethoxy, and nitro groups is interesting because of the centrosymmetric structure of 1 and the noncentrosymmetric structure of 2. The methylenedioxy group with a similar PPE contribution adopts a "zip-type" antiparallel planar arrangement:



an infinite chain of $R_2^2(8)$

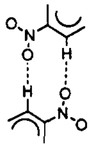
stabilized by the lateral C–H···O interactions in all the methylenedioxy compounds of Table 7.[36] However, such an arrangement may result in a centrosymmetric structure in the absence of any other group which can strongly influence the packing otherwise. In fact, all the methylenedioxy compounds listed in Table 7 are centrosymmetric.

In the crystal structures of TMAC and DNTM 2, the trimethoxyphenyl groups interact with one another.[41] The "template" with the relative orientations of the trimethoxyphenyl groups is shown as follows:

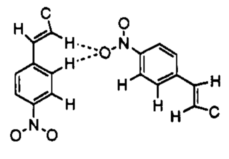


The trimethoxyphenyl units adopt a screw-related orientation with respect to each other and this orientation is in accordance with the requirements of a noncentrosymmetric structure. Such an arrangement could also adhere to the well-established Kitaigorodsky close-packing principle if one considers only size and shape factors.[42] It is also interesting to note that in DNTM 2 and TMAC, the PPE contribution by the three methoxy groups being the largest, is nearly the same indicating the significance of these interactions in stabilizing these structures.

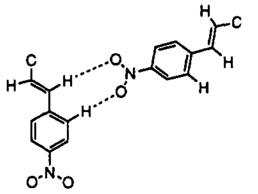
In the nitroaromatic compounds (R factor $\leq$ 0.05) retrieved from CSD, a centrosymmetric hydrogen bonded packing motif defined as in fragment 2 occurs 115 times with 2.54(18) Å as the mean O···H distance and 152(22)° as the mean C–H···O angle.[31,37] Even though there is a slight tendency for the nitro group to adopt a centrosymmetric packing, in the presence of more acidic hydrogens such as alkenic hydrogens, this hydrogen-bonding pattern is disturbed to a pattern similar to fragment 3 or 4 where the two molecular units may be screw/glide related.[35,43] In fact, the fragments 3 and/or 4 occur in all the dinitrophenyl compounds listed in Table 7.



$R_2^2(10)$
fragment 2



$R_2^1(7)$
fragment 3



$R_2^2(8)$
fragment 4

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(40) Bernstein, J. In *Organic Solid State Chemistry*; Desiraju, G. R., Ed.; Elsevier: Amsterdam, 1989. Desiraju, G. R. *Prog. Solid State Chem.* 1987, *17*, 295.

(41) Desiraju, G. R.; Kishan, K. V. R. *J. Am. Chem. Soc.* 1989, *111*, 4838.

(42) *Molecular Crystals and Molecules*; Kitaigorodsky, A. I., Ed.; Academic Press: New York, 1973.

(43) Pedireddi, V. R.; Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* 1992, 988.

In a layer, the methylenedioxyphenyl group has a greater tendency to generate a centrosymmetric pattern, while the trimethoxyphenyl group is adopting a motif defined by screw-related molecules. In nitroaromatics the situation is more complex and depends upon the availability of the number of acidic protons. In their absence, it tends to build a layer with centrosymmetric related units, but in their presence it seems to be generating a layer without center-of-inversion as in **1** and **2**. Now attention is focused to stacking these layers in an acentric fashion to generate a noncentrosymmetric crystal. If the molecules in a layer are highly planar and possess a high dipole moment, usually, it results in a centrosymmetric crystal optimizing the dipole–dipole along with a large number of C···C ($\pi\cdots\pi$) interactions across the stack. On the other hand, when the molecules are slightly nonplanar, such interactions are better optimized by the screw rather than inverse related molecules resulting in a noncentrosymmetric crystal. This rationale can be applied to explain the noncentrosymmetric structures of **2** and related molecules such as 2,6-dimethyl-4-hydroxy-4′-cyanoazobenzene,[16] 2-methoxy-4′-nitrostilbene,[44] 3-bromo-4′-(*N*,*N*-dimethylamino)-α-chlorostilbene,[3b] 4-nitro-4′-(*N*,*N*-dimethylamino)-α-cyanostilbene[45] and many others where the chirality has been achieved by the restricted rotation of dissymetric planes. A systematic study of these compounds can be useful in developing novel nonlinear optical materials.

Conclusions

The crystal structures of planar organic molecules containing a sufficient number of heteroatoms are characterized by the formation of layers. If the molecule has large hyperpolarizability, then the successive layers are inverse related optimizing dipole–dipole/charge-transfer interactions along with a large number of C···C ($\pi\cdots\pi$) interactions. This study suggests that the design of a noncentrosymmetric and efficient second harmonic generation organic crystal requires the achievement of two conditions. Recognition of specific functional groups which can adopt a screw/glide orientation in a layer constitutes the first and a small degree of molecular nonplanarity helping in the removal of inversion symmetry between the two highly overlapped molecules from adjacent layers is the second.

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Supplementary Material Available: Anisotropic atomic displacement parameters, bond lengths, bond angles, torsion angles, and structure factors (38 pages). Ordering information is given on any current masthead page.

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(44) Grubbs, R. B.; Marder, S. R.; Perry, J. W.; Schaefer, W. P. *Chem. Mater.* **1991**, *3*, 3.

(45) Tinant, B.; Touillaux, R.; Declercq, J. P.; Meerssche, M. V.; Leroy, G.; Weiler, J. *Bull. Soc. Chim. Belg.* **1983**, *92*, 403.

(46) Desiraju, G. R.; Kamala, R.; Kumari, B. H.; Sarma, J. A. R. P. *J. Chem. Soc., Perkin Trans. 2* **1984**, 181.

(47) Sarma, J. A. R. P.; Desiraju, G. R. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1187.

(48) Pedireddi, V. R.; Sarma, J. A. R. P.; Desiraju, G. R. *J. Chem. Soc., Perkin Trans. 2* **1992**, 311.

(49) Sharma, C. V. K.; Desiraju, G. R. Unpublished results.

(50) Sarma, J. A. R. P.; Desiraju, G. R. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1905.