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Hydrogen-Bond Formation in Nitroanilines: The First Step in Designing Acentric Materials

Thomas W. Panunto,[†] Zofia Urbánczyk-Lipkowska,[‡] Ruth Johnson,[§] and Margaret C. Etter*[†]

Contribution from the Chemistry Department, University of Minnesota, Minneapolis, Minnesota 55455. *Received April 1, 1987*

Abstract: Organizing molecules into predictable arrays is the first step in a systematic approach to designing organic solid-state materials. Intermolecular hydrogen bonds are an effective tool for organizing molecules, as exemplified by nitroaniline compounds, which associate via intermolecular hydrogen bonds between amino groups and nitro groups. From X-ray crystal structure data, infrared spectroscopy, and melting point data of a series of nitroanilines we have shown that intermolecular hydrogen bonds occur so frequently between amino and nitro groups that their existence in new structures can be used as a means for predicting packing patterns. The most common hydrogen-bond pattern in nitroanilines involves a three-center interaction with the amino proton located between the two "inside" lone pairs of electrons of a single nitro group. The geometry of this interaction, predictable within narrow limits, appears to be controlled by lone-pair directionality of the nitro groups. This directionality is observed even when the N(H)···O contacts exceed expected van der Waals distances. From analysis of the hydrogen-bond geometries of 28 nitroanilines and of 13 related compounds, the expected amino–nitro hydrogen-bond geometry has been determined, and the effect of this geometry on packing patterns has been analyzed. Hydrogen-bond rules have been derived for use in predicting the orientations of neighboring nitroaniline molecules. The implications of controlling nitroaniline packing patterns are explored in terms of designing potential nonlinear optical materials. The crystal structure of *N*-methyl-*p*-nitroaniline, the simplest of the nitroaniline compounds, was determined for use as a standard. Crystal data: monoclinic $P2_1/n$; a = 10.073 (3) Å, b = 6.930 (4) Å, c = 10.812 (3) Å, β = 101.95 (2)°, Z = 4, V = 735.6 (9) Å^3, R = 0.036 (599 reflections).

Since nitroanilines have inherently large second-order microscopic polarizabilities, they are good candidates for nonlinear optical materials.[1] Many of these compounds, however, exhibit no second harmonic generation (SHG) in the solid state, since they pack into centric crystal structures for which the macroscopic polarizability, $\chi(2)$ is necessarily zero.[2] Full realization of the potential usefulness of nitroanilines for SHG has been an elusive goal because of the difficulties of predicting and controlling crystal packing patterns.[3] The acentric crystal structures of most of the presently known organic nonlinear optical materials, including *p*-nitro-*o*-toluidine (commonly referred to as MNA), *m*-nitroaniline, and even urea, were found by chance. Molecular parameters such as meta-substitution,[4] vanishing dipole moments,[2c] chiral substitution,[3c] and hydrogen bonds[2d,e] have been invoked as ways to bias molecules to pack in acentric structures. In this paper we address one aspect of the problem of predicting and controlling crystal structures of nitroanilines, namely, the role of hydrogen-bond formation.

We have shown previously that hydrogen-bond interactions can play a more important role in controlling organic solid-state structures than their energies would indicate.[5] In this paper we show that the weak hydrogen-bond interactions between aniline donors and nitro acceptors can serve as primary determinants of the packing patterns of nitroanilines. We have analyzed the 28 crystal structures of nitroanilines reported in the literature, and also a series of closely related analogues, in order to determine the preferred geometric properties of NH···O hydrogen bonds in these compounds.

Criteria are established for using X-ray-derived bond lengths, orientational scatterplots, infrared frequency shifts, and melting point data for determining whether hydrogen bonds are present in nitroaniline structures. *We demonstrate that acentric hydrogen-bonded aggregates are a common structural feature of nitroaniline crystals even when their crystal structures are centric.* Nitroaniline hydrogen bonds prevent centers of symmetry from forming in the first step of the crystallization process. The polar molecular chains that form could be useful precursors for preparation of acentric nonlinear optical materials.[4]

Experimental Section

Materials. Compounds **1–3**, **6**, **7**, **10**, **12**, and **28** were purchased (Aldrich, purified by recrystallizations). Chemical structures were confirmed by solution infrared and NMR analyses to verify that the solids were not solvates, hydrates, or mixed crystals. Solid-state structures were confirmed by IR, melting point, and optical microscopic investigation of single-crystal morphologies, which appeared homogeneous. Our results were compared with reported literature data when available, and no unexpected polymorphs were found. *o*-Nitroaniline (**7**) is known to exist in three polymorphic forms,[6] but our recrystallization procedure followed known methods for preparing the γ form.[7] IR spectra were recorded on a Beckman 4250 grating spectrometer. Solid-state spectra were recorded as Nujol mulls, and solution spectra were run on 0.03–0.05 M chloroform solutions. Proton NMR spectra ($CDCl_3$ solutions) were recorded on an IBM NR300AF spectrometer at 300 MHz. Melting points were determined on a Fisher-Johns melting point apparatus.

Literature Search. The crystallographic and chemical literature were searched for crystal structures of small molecule nitroanilines by use of Molecular Structures and Dimensions,[8] Chemical Abstracts, and Acta Crystallographica. The search was verified by a Cambridge Crystallographic Data Base search (the data base was implemented after this paper had been prepared).[9] The results of the search are presented in

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[†] University of Minnesota.

[‡] Present address: Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland.

[§] Present address: Rochelle Crystal Corp., St. Paul, MN 55105.

(1) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690–703.

(2) (a) Zyss, J.; Oudar, J. L. *Phys. Rev.* **1982**, *A26*, 2016–2027. (b) Oudar, J. L.; Zyss, J. *Ibid.* **1982**, *A26*, 2028–2048. (c) Zyss, J.; Chemla, D. S.; Nicoud, J. F. *J. Chem. Phys.* **1981**, *74*, 4800–4811. (d) Zyss, J.; Nicoud, J. F.; Coquillay, M. *J. Chem. Phys.* **1984**, *81*, 4160–4167. (e) Zyss, J.; Berthier, G. *J. Chem. Phys.* **1982**, *77*, 3635–3653.

(3) (a) Meredith, G. R. In *Nonlinear Optical Properties of Organic and Polymeric Materials*; Williams, D. J., Ed.; ACS Symposium Series 233; American Chemical Society: Washington, DC, 1983; pp 27–56. (b) Badan, J.; Hierle, R.; Perigaud, A.; Zyss, Z. *Ibid.* pp 81–107. (c) Nicoud, J. F.; Twieg, R. J. In *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D., Zyss, J., Eds.; Academic: Orlando, FL, 1986; pp 227–296.

(4) Curtin, D. Y.; Paul, I. C. *Chem. Rev.* **1981**, *81*, 525–541.

(5) (a) Etter, M. C. *Isr. J. Chem.* **1985**, *25*, 312–319. (b) Etter, M. C. *J. Am. Chem. Soc.* **1982**, *104*, 1095–1096.

(6) Dhaneshwar, N. N.; Tavale, S. S.; Pant, L. M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 2507–2509.

(7) Herbstein, F. H. *Acta Crystallogr.* **1965**, *19*, 590–595.

(8) *Molecular Structures and Dimensions*; Crystallographic Data Centre, Cambridge and the International Union of Crystallography, University Press: Cambridge, England, 1935–1983.

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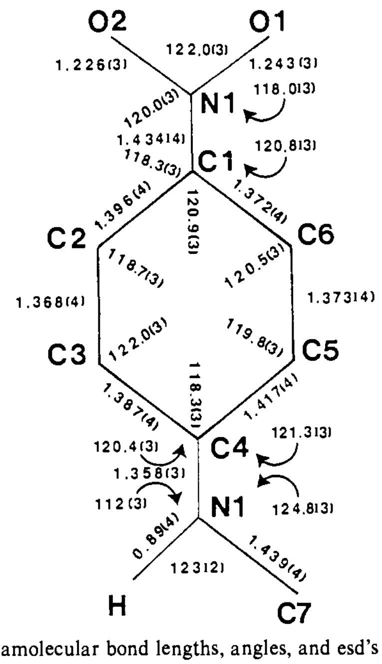

Figure 1. Intramolecular bond lengths, angles, and esd's for *N*-methyl-*p*-nitroaniline (**1**).

Tables I and II and in the supplementary material.

Molecular Graphics. Pictures of hydrogen-bonded substructures of each nitroaniline crystal structure were prepared with CHEM-X, a molecular modeling and graphics program,[10] run on a Lundy 5688 color graphics terminal. Input data consisted of atomic coordinates from the literature for each compound for which an X-ray crystal structure had been reported. The crystal structure data were uncorrected, with the reported R values varying from 0.036 to 0.145. Owing to the relatively small number of structures available, all data were used. No attempt was made to improve the data by lengthening the N–H bonds[11] or by adding missing hydrogen atoms. Obvious positional errors found in literature values are noted in the tables.

X-ray Structure Analysis of *N*-Methyl-*p*-nitroaniline. A single crystal (0.8 × 0.5 × 0.3 mm) of *N*-methyl-*p*-nitroaniline (**1**) grown from ethanol solution was used for data collection. Monoclinic unit cell parameters obtained by least-squares fit of 25 reflections in the θ range 5–18° gave the following: a = 10.073 (3), b = 6.930 (4), c = 10.812 (3) Å; β = 101.95 (2)°; V = 735.6 (9) Å^3; space group $P2_1/n$; Z = 4. Data collection conditions: Enraf-Nonius CAD4 diffractometer; θ–2θ scan mode; filtered Mo Kα radiation (λ = 0.7108 Å, μ = 0.96 cm^{-1}). A total of 1447 independent reflections were measured up to θ = 26°. The number of observed reflections was 599, with $I > 3\sigma(I)$.

The structure was solved by direct methods and refined with anisotropic thermal parameters to R = 0.072. Atomic positions for *N*-methyl and amino hydrogens were found from difference maps, and their positional and isotropic thermal parameters were refined. Positions for the remaining four hydrogens were calculated. Refinement, based on F, converged at R = 0.036 and R_w = 0.044 for 599 reflections with $F_o > 3\sigma(F_o)$. Esd's of a unit weight observation were 1.237, with maximum shift/error 0.22. All calculations were performed on a PDP 11/34 computer. Structure determination programs (including MULTAN 80) and atomic scattering factors were used as implemented in the Structure Determination Package.[12] Positional parameters are given in Table III. Thermal parameters, F_o/F_c, and inter- and intramolecular distances and esd's are available as supplementary material.

Results

Molecular and Crystal Structure of 1. *N*-Methyl-*p*-nitroaniline is useful as a reference compound, since it contains only one proton donor (NH) and a single nitro group acceptor. The molecules are nearly planar, with the $NHCH_3$ and NO_2 groups rotated 2.0 and 2.4°, respectively, out of the plane of the aromatic ring. Selected intramolecular bond lengths and angles shown in Figure 1 reflect the conjugated character of the structure with the amino and nitro C–N bond lengths showing partial double-bond character.

The molecules are held together by hydrogen bonds formed between the amino and nitro groups on neighboring glide-related molecules. The geometry of the interaction is given in Table I. The amino proton of **1** is located between the two oxygens of the neighboring nitro group in a position where the proton could interact with both oxygens simultaneously. The distances between the amino nitrogen and the nitro oxygens are 3.062 (4) and 3.473 (4) Å, and the two NH proton to nitro oxygen distances are 2.31 (4) and 2.61 (4) Å. On the basis of distance criteria alone, the second of these interactions would not be called a hydrogen bond, since the distance is greater than the sum of the van der Waals radii of hydrogen and oxygen (2.5 Å).[13]

Hydrogen-bond interactions in **1** result in formation of infinite planar and polar chains oriented parallel to the (101) plane, as shown in the stereoview in Figure 2. Neighboring chains are inversion related with the nitro group of one molecule located parallel to and overlapping a neighboring phenyl ring (interplanar spacing 3.50 Å).

Hydrogen-Bond Geometry and Hydrogen-Bond Patterns of Nitroanilines. An analysis of the hydrogen-bond patterns of all available nitroaniline structures from the literature was carried out to determine the role of hydrogen bonds in the packing patterns of these compounds and to identify recurring patterns that would be useful in predicting crystal structures. For each compound, the shortest intermolecular distance between an amino nitrogen and a nitro oxygen [N(H)···O], referred to as the primary interaction, was identified, and the bond lengths and angles associated with this interaction were calculated. No constraints were put on allowed N(H)···O distances, but we used only those interactions occurring in the forward direction (i.e., on the proton side of the N–H bond and on the oxygen side of the –N–O bond). For primary amines, the bond distances and angles associated with the interactions of the second proton, called the secondary interactions, were also calculated. Table I gives the symmetry relations of hydrogen-bonded nitroaniline molecules, crystal space groups, hydrogen-bond geometries, and nitro and amino group torsion angles. Representative data for related compounds are given in Table II.

The hydrogen-bond data are given in Figure 3 in a scatterplot diagram that shows the positions of protons from the primary and secondary N···O hydrogen bonds. Distances of the proton from the nitro plane (D values) are <1.0 Å for primary interactions and <1.8 Å for secondary interactions.

The most common mode of association of primary nitroanilines involves an amine–nitro interaction with the amino proton positioned between the two oxygens of a single nitro group and the N–O···H angle close to or less than 130°. The second proton forms either an intramolecular hydrogen bond to an ortho substituent or an intermolecular hydrogen bond to a neighboring chain. The interchain bonds have much more relaxed geometrical constraints than the "inside" hydrogen bonds, as seen by the larger scatter in Figure 3. The precise geometry of the inside hydrogen bonds probably reflects a compromise between formation of an optimum geometry for the three-center primary bond and formation of optimum geometry for the interchain bond.

The structural consequences of the NH···O interactions are seen in Figure 4, which shows the *preferential ordering of neighboring nitroaniline molecules into polar chains*. The simplest chain structure, shown for **1**, Figure 4a, has inside hydrogen bonds and molecules associated into a polar array. Secondary amines **4**, **5**,

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(9) *Cambridge Structural Database*; Cambridge Crystallographic Data Centre, University Chemical Laboratory: Cambridge, England, Version I (VAX), September 1986 update.

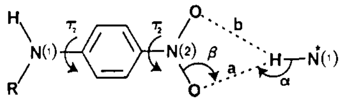
(10) Davies, E. K., CHEM-X, Chemical Crystallography Laboratory, Oxford University; developed and distributed by Chemical Design, Ltd., Oxford, England, 1986 update.

(11) Taylor, R.; Kennard, O. *Acc. Chem. Res.* **1984**, *77*, 320–326.

(12) Frenz, B. A. *Enraf-Nonius Structure Determination Package*, 4th ed.; B. A. Frenz, Associates: College Station, TX, 1982.

(13) The sum of the van der Waals radii of O and N is 3.20 Å (N = 1.70, O = 1.50 Å) if computed from Bondi's values and 3.14 Å (N = 1.60, O = 1.54 Å) if computed from Nyburg's values. The van der Waals radius of hydrogen is taken as 1.0 Å, from Bondi. (a) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451. (b) Nyburg, S. C.; Faerman, C. H. *Acta Crystallogr., Sect. B: Struct. Sci.* **1985**, *B41*, 274–279.

Table I. Geometry of Intermolecular Amino–Nitro Contacts for Nitroanilines[a]



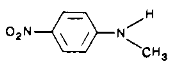
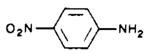
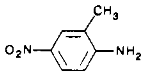
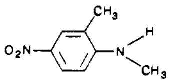
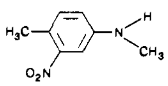
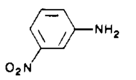
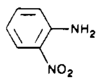
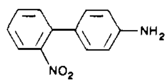
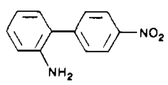
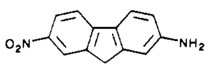
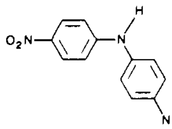
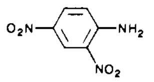
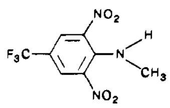
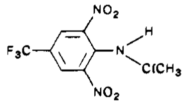
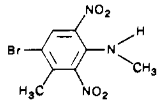
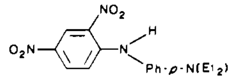
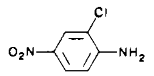
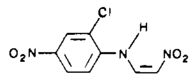
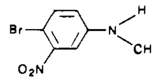
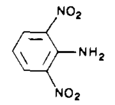
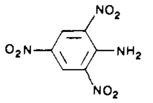
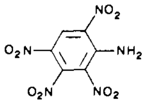
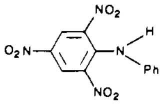
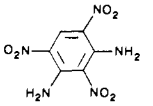
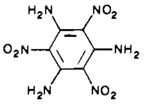
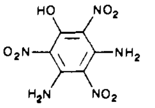
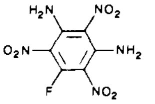
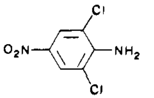
no.	compd	space group	R	symmetry relation	N(H)···O, Å	1°/2°[b]	length, Å		angle, deg		τ value, deg		D	ref[f]
							a	b	N–H···O	N–O···H	τ_1	τ_2		
1		$P2_1/n$	0.036	glide	3.062 (4)	1°	2.31 (4)	2.61 (4)	142	100	2.0	2.4	0.17	a
2		$P2_1/n$	0.095	glide	3.07	1°	2.34	3.22	164	118	10.6	2.0	0.76	b
				glide	3.14	2°	2.35	4.73	139	154	10.6	2.0	0.93	
3		Ia	0.040	glide	3.117 (4)	1°	2.33 (4)	2.83 (4)	176	107	6.8	1.1	0.08	c
				glide	3.234 (4)	2°	2.51 (6)	4.46	143	221	6.8	1.1	1.38	
4		$Pna2_1$	0.056	glide	3.019 (6)	1°	2.24 (5)	2.91 (5)	130	111	2.3	1.4	0.15	d
5		$P2_1/c$	0.080	translation	3.08	1°	2.14	2.88	167	114	5.62	12.95	0.25	e
6		$Pbc2_1$	0.084	translation	3.250	1°	2.30	2.55	159	99	0.8	2.5	0.16	f
				glide	3.317	2°	2.69	3.39	119	110	0.8	2.5	1.75	
7		$P2_1/a$	0.109	inversion	A, 3.00	1°	2.08	3.27	146	125	13.4	2.2	0.73	g
					B, 3.02	1°	2.25	3.17	139	120	20.1	3.7	0.78	
8		$P2_1/c$	0.045	glide	3.16	1°	2.33 (5)	4.33	144	129	0.7	34.6	0.84	h
				glide	3.27	2°	2.39 (5)	2.53	150	96	0.7	34.6	0.38	
9		$C2/c$	0.102	inversion	3.310 (8)	1°						7.1 (6)		l
10		$P2_1/n$	0.043	translation	3.07	1°	2.52 (3)	2.48 (3)	116	90	5.4	5.7	0.88	h
11		$P2_1/n$	0.039	glide	3.203 (2)	1°	2.43 (2)	4.27	158	159	23.2	1.5	0.85	j
12		$P2_1/c$	0.063	translation	3.00	1°	2.58	3.83	102	133	2.7 (5)	6.6 (4)	0.56	k
				screw	3.05	2°	1.97[e]	3.05	173	124	2.7 (5)	4.3 (4)	0.46	
13		$P2_1/c$	0.067	asymmetric units	A, 3.21	1°	3.35[c]	4.15	73	108	47	2	2.89	l
					B, 3.22	1°	2.32[c]	3.84	148	145	22	6	0.81	
14[d]		$P2_12_12_1$	0.11	screw	3.61									m
15		$P\bar{1}$	0.082	inversion	3.13	1°						6		n
16		$P2_1/c$	0.13	inversion	3.39	1°						6		o
17		$Pna2_1$	0.103	glide	3.047	1°						3		p
18[d]		$P2_1/c$	0.055	translation	4.72		3.66	5.79	164	201	7.6 (9)		0.33	q
19		$P2_1/c$	0.145	glide	3.05	1°						3.1		e

Table I (Continued)

no.	compd	space group	R	symmetry relation	N(H)···O, Å	1°/2° [b]	length, Å		angle, deg		τ value, deg		D	ref [f]
							a	b	N–H···O	N–O···H	τ_1	τ_2		
20		$P2_1/c$	0.056	glide	3.00	1°	2.65	3.51	101	123	6.2	5.2	0.22	r
				glide	3.22	1°	2.51	2.86	135	105	6.2	5.2	0.18	
21		$P2_1/c$	0.084	glide	3.03	1°	2.36	2.80	133	104	1.9	3.8	0.49	s
				inversion	3.15	2°	2.38	4.03	141	155		8.5	0.21	
22		$P2_1/c$	0.08	glide	3.09	1°	2.39	2.50	129	94	5	19	0.35	t
				screw	3.09	1°	2.42	3.06	129	110	5	3	0.29	
23		$P2_1/c$	0.12	glide	3.12	1°						7		u
24		Pc	0.103	translation	2.97	1°						4.6		v
				translation	2.99	1°						4.6		
25		$P\bar{1}$	0.053	translation	2.930 (6)	1°	2.24 (8)	3.04	121	119	1.5	3.67	0.29	w
				translation	2.934 (6)	1°	2.35 (9)	3.07	119	117	6.5	3.24	0.07	
				translation	2.960 (6)	1°	2.37 (6)	2.96	125	114	5.9	1.40	0.25	
				translation	2.989 (6)	1°	2.39 (7)	2.84	136	108	1.5	3.67	0.21	
				translation	2.993 (6)	1°	2.37 (8)	2.91	129	111	6.5	3.24	0.01	
				translation	2.995 (6)	1°	2.40 (6)	3.00	126	112	5.9	1.40	0.08	
26 [e]		$P2_12_12_1$	0.044	screw	2.94	1°	2.35 (7)	3.00	125	113	4	15	0.00	x
				translation	2.99	1°	2.22 (7)	2.82	150	108	17	8	1.00	
				screw	3.01	1°	2.30 (7)	2.99	120	114	4	15	0.11	
27		Pc	0.040	screw	2.99 (1)	1°	2.27 (8)	2.88	124	111	1.4	23.2 (8)	0.25	y
				translation	3.07 (1)	1°	2.37 (12)	3.01	125	111	0.7	17.8 (8)	0.67	
				translation	3.08 (1)	1°	2.43 (14)	3.13	118	116	0.7	17.8 (8)	0.12	
28		$P2_1/c$	0.038	screw	3.003 (6)	1°	2.24 (5)	3.18	148	120 (4)	6.3	7.2	0.35	z

[a] Geometrical values taken from the references were used with their esd's if provided; otherwise, distances (Å) and τ values (deg) were calculated to the hundredths place, and angles, to the tenths. Intramolecular interactions are not included. [b] Type of hydrogen bond; 1° for primary interaction (the shortest intermolecular amino nitrogen to nitro oxygen contact) and 2° for secondary interaction. [c] Reported values for these hydrogen atom positions are incorrect and are not used in our calculations or graphs. [d] Compounds **14** and **18** are considered to have no intermolecular hydrogen bonds, so their hydrogen atoms are not used in any calculation or graph. [e] Since the phenolic hydrogen of **26** is involved only in an intramolecular hydrogen bond, this compound behaves like a nitroaniline structure, so it is included in the nitroaniline tabulation. [f] References: (a) This work. (b) Trueblood, K. N.; Goldish, E.; Donohue, J. *Acta Crystallogr.* **1961**, *14*, 1009–1017. (c) Lipscomb, G. F.; Garito, A. F.; Narang, R. S. *J. Chem. Phys.* **1981**, *75*, 1509–1526. (d) Twieg, R. J., IBM, personal communication. (e) Chiaroni, A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1971**, *B*27, 448–458. (f) (i) Shapski, A. C.; Stevenson, J. L. *J. Chem. Soc. Perkin Trans. 2* **1973**, 1197–1200. (ii) Ploug-Sorensen, G.; Andersen, E. K. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 1813–1815. (g) Dhaneshwar, N. N.; Tavale, S. S.; Pant, L. M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 2507–2509. (h) Fallon, L., III; Ammon, H. L. *J. Cryst. Mol. Struct.* **1974**, *4*, 63–75. (i) Sutherland, H. H.; Ali-Adib, Z. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 432–433. (j) Hardgrove, G. L., Jr.; Einstein, J. R.; Wei, C. H. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 616–620. (k) Prasad, L.; Gabe, E. J.; LePage, Y. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 674–675. (l) Brown, J. N.; Towns, R. L. R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 149–151. (m) Towns, R. L. R.; Brown, J. N.; Giam, C. S. *Cryst. Struct. Commun.* **1975**, *4*, 543–546. (n) Abrahamsson,S.; Innes, M.; Lamm, B. *Acta Chem. Scand.* **1967**, *21*, 224–232. (o) Shvets, A. E.; Bleidelis, Y. Y.; Freimanis, Y. F. *J. Struct. Chem.* (*Engl. Trans.*) **1974**, *15*, 430–433. (p) McPhail, A. T.; Sim, G. A. *J. Chem. Soc.* **1965**, 227–236. (q) Simonsen, O. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 2060–2062. (r) Parkanyi, L.; Kalman, A. *J. Mol. Struct.* **1984**, *125*, 315–320. (s) Holden, J. R.; Dickinson, C.; Bock, C. M. *J. Phys. Chem.* **1972**, *76*, 3597–3602. (t) Dickinson, C.; Stewart, J. M.; Holden, J. R. *Acta Crystallogr.* **1966**, *21*, 663–670. (u) Divjakovic, V.; Nowacki, W.; Edenharter, A.; Engle, P.; Ribar, B.; Halasi, R. *Cryst. Struct. Commun.* **1973**, *3*, 411–413. (v) Holden, J. R. *Acta Crystallogr.* **1967**, *22*, 545–550. (w) Cady, H. H.; Larson, A. C. *Acta. Crystallogr.* **1965**, *18*, 485–496. (x) Bhattacharjee, S. K.; Ammon, H. L. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 2082–2085. (y) Ammon, H. L.; Bhattacharjee, S. K.; Holden, J. R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 1851–1854. (z) Hughes, D. L.; Trotter, J. *J. Chem. Soc. A* **1971**, 2181–2184.

11, **19**, and **23** have just one proton to donate for hydrogen bonding, and their chain structures are very similar to that of **1**.

The primary polar chains of *p*-nitroaniline (**2**) are formed by an inside hydrogen bond as for **1** (Figure 4b). The chains are further associated by a second longer NH···O contact that occurs between the glide-related chains. This two-dimensional hydrogen-bonded plane then packs with the next layer by inversion symmetry to give a centric structure. Chemical and spectroscopic results presented below confirm the presence of at least one hydrogen bond in **2**.

p-Nitro-*o*-toluidine (**3**) has a polar hydrogen-bonded chain very much like that of **2**, although the hydrogen-bond distances in **3** are longer than in **2** (Figure 4c). The polar chains in **3** are held together by a long hydrogen bond [3.117 (4) Å], and they are

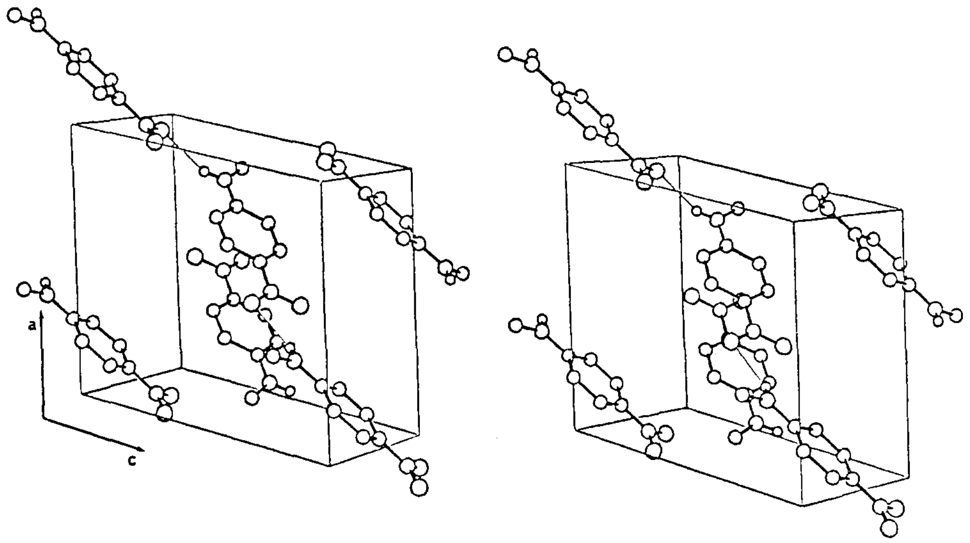


Figure 2. ORTEP stereoview of *N*-methyl-*p*-nitroaniline (**1**) viewed along (010). Hydrogen bonds, indicated by thin lines, occur between glide-related molecules in polar hydrogen-bonded chains extending along (101).

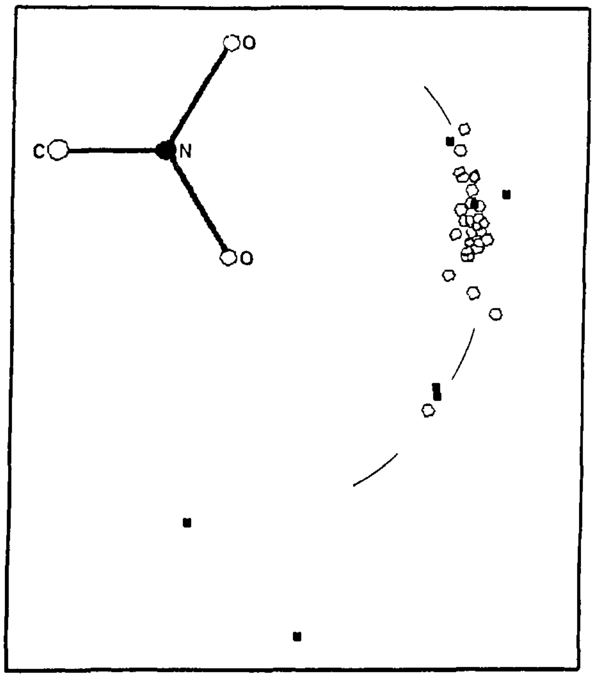


Figure 3. Scatterplot of amino hydrogen donor positions relative to nitro acceptor group. The circles represent hydrogen atoms of primary –N–O···H–N– contacts in each nitroaniline structure from Table I. The blocks represent hydrogen atoms involved in secondary –N–O···H–N– contacts. The expected van der Waals contact distance for oxygen and hydrogen (2.5-Å spacing[13a]) is shown by an arc.

connected by a long intermolecular NH···O contact [3.234 (4) Å]. Its acentric crystal-packing pattern arises from the packing of neighboring chains by translation symmetry rather than about inversion centers.

m-Nitroaniline (**6**), which forms an acentric crystal structure, also has two very long NH···O interactions (both >3.2 Å), one of which is inside (Figure 4f). Melting point and spectroscopic evidence demonstrate that at least one of these interactions is a hydrogen bond. The hydrogen-bond strengths are weak, consistent with the expected weak proton-donating and -accepting strengths of meta-substituted compounds. Compound **5**, which also has a *m*-nitro group, has shorter hydrogen-bond distances than **6** but longer than **1**. The length of the contacts in **5** is surprising, since the nitro group is twisted out of the aromatic plane by 13°.

The asymmetric unit of *o*-nitroaniline (**7**) has two molecules (A and B), each of which has an intramolecular hydrogen bond (Figure 4g). The other amino hydrogen in each molecule forms polar chains of alternating A and B molecules with two NH···O hydrogen bonds in the chain corresponding to A···B and B···A contacts. These primary hydrogen bonds are essentially the same length, and both are inside.

Compounds **8**–**11** have more complex molecular structures than the nitroanilines discussed so far, yet the hydrogen-bond interactions between their nitro and amino groups still serve to orient the molecules into predictable polar arrays (Figure 4). Compound **8** is of particular interest because of the nonplanarity of the biphenyl structure, which should cause less conjugation between the amino and nitro groups and make hydrogen bonding less likely. The orientation of neighboring molecules and the lengths of their NH···O contacts, however, indicate that hydrogen bonding occurs.

Polar arrays are also found for compounds **12** and **20**–**27**, which have multiple nitro acceptors and intramolecular hydrogen bonds. The proton involved in the intramolecular hydrogen bond is participating in a four-center interaction. In **12** the amino hydrogen that is not involved in an intramolecular bond forms an intermolecular hydrogen bond to a 2-NO_2 group and another to a 4-NO_2 group.

Four-center interactions are also found in **13**, **15**, and **16**, but they lead to dimers rather than polymer chains. Ortho-substituted nitroanilines can act as proton donors and as proton acceptors to a single neighboring molecule [although *o*-nitroaniline (**7**) itself does not do this]. Since the dimers that result are centric or pseudocentric, ortho-substituted nitroanilines are not good choices for designing acentric crystals (Figure 5).

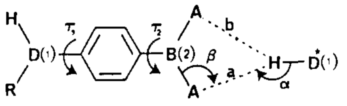
Compounds **14** and **18** are the only nitroanilines that do not form any intermolecular hydrogen bonds. The bulky *tert*-butyl group in **14** may sterically hinder the approach of acceptor groups and prevent formation of hydrogen bonds to the amino proton. In **18**, the amino proton forms two intramolecular H bonds, so it is effectively shielded from intermolecular interactions.

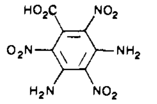
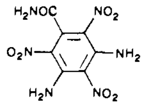
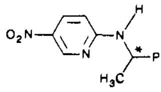
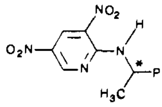
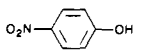
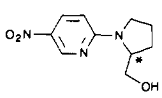
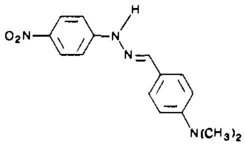
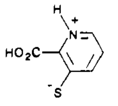
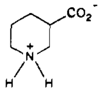
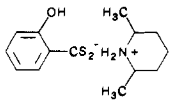
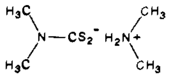
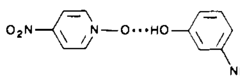
Compounds **25**–**27** are different from the other compounds studied, since both protons form inside bonds to the same nitro group on a neighboring molecule. Remarkably, the hydrogen-bond geometry is very similar to that in monodentate contacts, with each proton positioned close to both nitro lone pairs of electrons.

In **25** the intermolecular hydrogen bonds occur between an amino group and its corresponding *p*-nitro group on a neighbor. Since there are three such interactions, three polar chains are formed at approximately 120° to each other. The resulting plane of molecules is polar by virtue of the slight deviations from threefold symmetry. The overall three-dimensional structure is strictly centric, since neighboring planes are related by inversion centers.

In compound **26**, a phenol analogue of **25**, one amino group donates a proton to the corresponding *p*-nitro group on a neighboring molecule, and the other amino group donates both of its

Table II. Geometry of Intermolecular Amino–Nitro Contacts for Nitroaniline Analogues[a]



no.	compound	space group	R	symmetry relation	D(H)···O, Å	1°/2°	length, Å		angle, deg		τ value deg		D	ref[b]
							a	b	D–H···A	B–A···H	τ_1	τ_2		
29		$P2_1/c$	0.039	glide screw	2.964 (3) 3.018 (3)	1° 1°	2.27 (3) 2.33 (3)	4.17 2.66	138 132	129 101	7.8 10.6	22.0 (3) 14.6 (3)	1.38 0.79	a
30		$P2_1/n$	0.036	glide	3.02	1°	2.43 (3)	2.89	122	107	6.8	34.8 (2)	0.33	b
31		$P2_1$	0.041	translation	3.06	1°	2.17 (4)	4.13	164	163	9.6	3.0	0.59	c
32		$P2_1$	0.052	translation	3.13	1°	2.46	3.96	128	132	4.3	9.3	1.72	c
33		$P2_1/n$	0.083	glide	2.818 (6)	1°	2.19	2.75	117.3 (4)	105.4 (4)		1.53	0.69	d
34		$P2_1/a$	0.069	glide	2.84	1°	2.04	2.86	124.4	116.0		1.53	0.39	e
35		$P2_1$	0.047	screw	2.965 (4)	1°	2.20 (10)	2.63 (10)	168	103		8.9	0.41	c
36		$P2_12_12_1$	0.112	screw screw	A, 3.01 B, 3.31	1° 1°	2.03 2.35	3.21 2.45	164 154	123 92	2.24 3.65	10.5 4.8	0.10 0.35	f
37		$P2_1$	0.029	screw	2.826 (4)	1°	2.05 (4)	2.97	137.0 (25)	117.0 (25)		4.1 (3)	0.63	g
38		$Pna2_1$	0.033	glide glide	2.695 (3) 2.723 (3)	1° 2°	1.79 (3) 1.86 (3)	2.72 3.91	163 (2) 164 (3)	112.959 234			0.08 0.77	h
38		$Pna2_1$	0.080	– screw	3.355 (9) 3.375 (9)	1° 1°	2.315 (12) 2.489 (12)	4.58 2.504 (13)	165.8 (7) 142.3 (7)	107.2 (5) 84.3 (4)		5.4 5.4	1.85 0.40	i
40		$P2_1/c$	0.053	screw –	3.326 (3) 3.343 (2)	1° 1°	2.46 (3) 2.61 (3)	2.99 (3) 2.66 (3)	157 138	89 80			1.53 1.52	j
41		Cc	0.044	translation mirror	3.13 3.18	1° 2°						4.0 40		k

[a] Geometrical parameters defined as in Table I. D in D(H)···O and D–H···O represents the donor atom. A in B–A···H represents the acceptor atom that is bonded to B. The torsion angles of the donor and acceptor groups, relative to the aromatic ring, are τ_1 and τ_2, respectively. [b] References: (a) Ammon, H. L.; Prasad, S. M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 921–924. (b) Ammon, H. L.; Bhattacharjee, S. K. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 2083–2086. (c) Twieg, R. J., IBM, personal communication. (d) Coppens, P.; Schmidt, G. M. J. *Acta Crystallogr.* **1965**, *18*, 62–67. (e) Coppens, P.; Schmidt, G. M. J. *Acta Crystallogr.* **1965**, *18*, 654–663. (f) Brown, J. N.; Kutchan, T. M.; Rist, P. E. *Cryst. Struct. Commun.* **1980**, *9*, 17–22. (g) Bourne, P. E.; Taylor, M. R. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 266–268. (h) Brehm, L.; Krogsgaard-Larsen, P.; Johnston, G. A. R.; Schaumberg, K. *Acta Chem. Scand., Ser. B* **1976**, *B30*, 542–548. (i) Van Roey, P.; Kerr, K. A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 1679–1685. (j) Wahlberg, A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 3392–3395. (k) Lechat, J. R.; de Almeida Santos, R. H.; Bueno, W. A. *Acta. Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 1468–1470.

protons to intramolecular *o*-nitro groups. Thus, two polar hydrogen-bonded chains are formed. They pack by screw-axis symmetry, so the overall structure is acentric. The phenol proton forms only an intramolecular hydrogen bond. Compound **27**, a fluoro analogue of **25**, has the same hydrogen-bond pattern as phenol **26** except for the internal phenol hydrogen bond.

Compounds **20–23** and **28** are nitroaniline derivatives that have two acceptor groups in the positions ortho to the amino function. In **20–23** they are nitro groups, and in **28** the ortho groups are chlorines. In each case the two amino protons are internally hydrogen bonded. In **21–23** they form four-center bonds with intermolecular contacts to both *o*- and *p*-nitro groups on neigh-

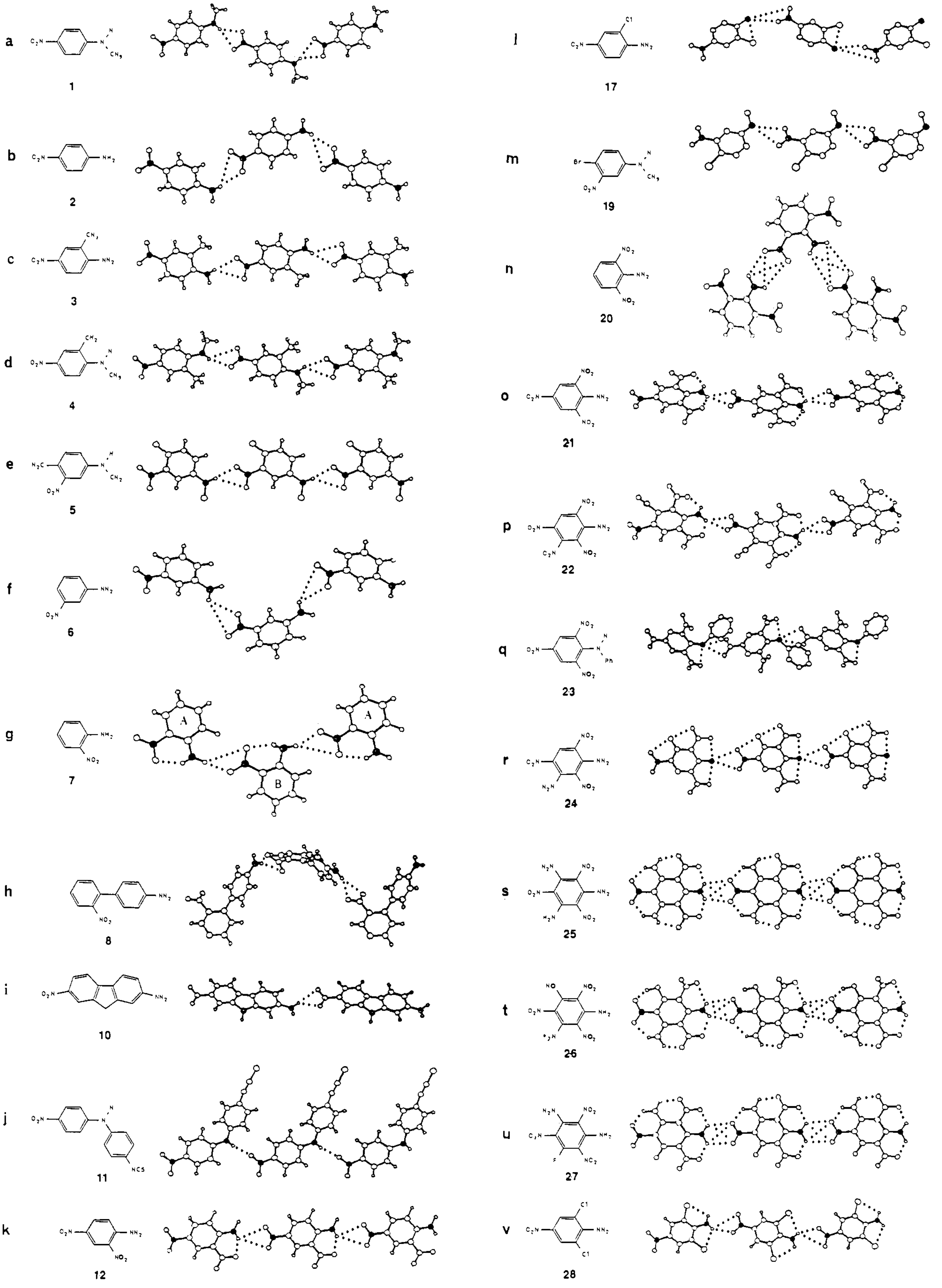


Figure 4. Polar hydrogen-bonded chain structures of nitroaniline compounds. The primary –NH···ONO contact and the intramolecular hydrogen bonds are shown as dotted lines. The polar polymeric chains are drawn as found in their respective crystal structures. Only one of the asymmetric units is shown for *o*-nitroaniline (7).

Table III. Atomic and Positional Parameters and Their Estimated Standard Deviations for *N*-Methyl-*p*-nitroaniline (**1**)[a]

atom	x	y	z	B, Å^2
C1	0.1123 (2)	0.1748 (4)	0.1262 (2)	4.25 (6)
C2	0.1421 (2)	−0.0185 (4)	0.1350 (2)	4.51 (6)
C3	0.2207 (3)	−0.1008 (4)	0.0595 (2)	4.46 (6)
C4	0.2730 (2)	0.0153 (4)	−0.0271 (2)	3.94 (6)
C5	0.2414 (3)	0.2104 (4)	−0.0331 (2)	4.91 (6)
C6	0.1621 (3)	0.2920 (4)	0.0414 (3)	5.00 (7)
C7	0.3849 (3)	−0.2627 (5)	−0.1081 (3)	6.43 (8)
N1	0.0263 (2)	0.2606 (4)	0.2015 (2)	5.54 (6)
N2	0.3502 (2)	−0.0616 (3)	−0.1038 (2)	5.13 (5)
O1	−0.0029 (2)	0.4323 (3)	0.1894 (2)	7.91 (6)
O2	−0.0156 (2)	0.1565 (4)	0.2786 (2)	7.46 (6)
H(N)*	0.377 (3)	0.028 (5)	−0.152 (2)	8.5 (8)
H71*	0.444 (3)	−0.276 (4)	−0.163 (3)	9.5 (9)
H72*	0.433 (2)	−0.311 (4)	−0.027 (2)	7.3 (7)
H73*	0.303 (3)	−0.341 (5)	−0.132 (3)	10.4 (9)
H21*	0.108	−0.095	0.194	5.7 (6)
H31*	0.240	−0.236	0.065	5.0 (6)
H51*	0.275	0.290	−0.091	5.6 (6)
H61*	0.142	0.427	0.036	6.0 (6)

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

boring molecules, while compound **20** participates in external contacts only to *o*-nitro groups. Compound **28** has one proton involved in a four-center interaction to the *p*-nitro group of a neighbor, while the other proton forms no intermolecular hydrogen bonds. Compared with **21**, **22** has one additional nitro group, meta to the amino function, that is not used for hydrogen bonding (it is twisted 64° out of the plane of the ring). The hydrogen-bond patterns of **21** and **22** are identical.

Hydrogen atom positions were not available for several compounds in Table I, so a detailed analysis of their hydrogen-bond patterns is not possible. Nevertheless, the N···O distances between nearest neighbor nitro and amino groups and the aggregate patterns shown in Figure 4 show that hydrogen-bond interactions occur in these compounds with approximately the same geometry as in the other nitroanilines.

Hydrogen-Bond Patterns of Nitroaniline Analogues. Compounds **29–41** (Table II) were chosen to demonstrate how knowledge of preferred hydrogen-bond patterns of nitroanilines can be applied to analysis and prediction of hydrogen-bond patterns of related compounds. Compounds **29** and **30** have nitroaniline groups plus either a carboxylic acid or amide function, both of which can form strong hydrogen bonds that could compete with and possibly prevent the formation of nitroaniline-type hydrogen bonds. In **29** the normal carboxylic acid dimers and the normal nitroaniline hydrogen-bond patterns form independently of one another (Figure 6a). In **30**, however, the nitroaniline groups have disrupted the expected amide dimers, since the amide group acts as an oxygen acceptor for one proton from an amino group (intermolecular) and as a proton donor to the *p*-nitro groups of two other neighboring molecules (Figure 6b). Nitro groups, alone, rather than ones conjugated to anilines, do not compete favorably with formation of amide dimers, since in *p*-nitrobenzamide the normal amide dimer pattern is observed, and the nitro group serves as an acceptor for the second amide proton.[14] It is surprising that in **30** a nitro–amide hydrogen bond prevails over the expected amide dimer, since a nitro–amide interaction is expected to be weaker. Comparison of the hydrogen-bond lengths in these structures shows that amide–nitro hydrogen bonds actually are longer than hydrogen bonds in amide dimers. The N···O and N(H)···O bond lengths for the amide–amide hydrogen bond in *p*-nitrobenzamide are 2.910 (2) and 2.03 (3) Å. The N···O and N(H)···O bonds for amide–nitro interactions in *p*-nitrobenzamide are 3.220 (2) and 2.34 (3) Å, and in **29** the two such interactions are 3.16, 2.61 (3), and 3.21, 2.30 (3) Å, respectively.

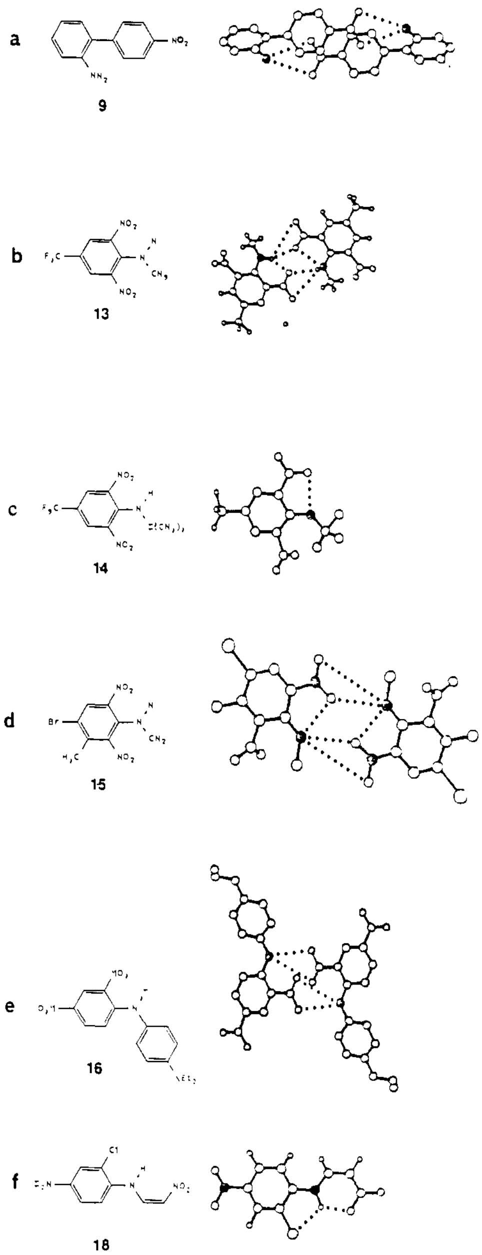


Figure 5. Hydrogen-bond patterns of nitroanilines that do not form polymeric chains. When an amino group is ortho to a nitro group, intermolecular hydrogen bonds can cause formation of centric or pseudocentric dimers, as in **9**, **13**, **15**, and **16** above. In **14** and **18** no intermolecular hydrogen bonds are formed.

Compounds **31** and **32** are pyridine analogues of nitroanilines. They both form polar chains from hydrogen bonds between the amino proton and the *p*-nitro groups. Bulky chiral substituents appear to have distorted the geometry of this interaction, so the intermolecular hydrogen bonds have N–H···O angles greater than 130°. These protons are probably interacting with only one of the nitro group inside lone pairs of electrons.

Compounds **33–40** are analogues of nitroanilines in which isographic substitutions have been made for either the aniline or the nitro group. Isographic groups are ones that have the same number of proton donors (or acceptors) available for hydrogen bonding, so they can be substituted for one another while preserving a particular hydrogen bond pattern.[4] Thus, **33–36** are isographic with secondary anilines since the hydroxyl and hydrazone functional groups supply just one proton, and **37–40** are isographic with nitro compounds because they have CO_2H, CS_2^-, and CO_2^- groups that can provide two acceptor sites for protons. In each case a three-center inside interaction takes place to give polar chains (Figure 6). The hydrogen bond lengths for **33**, **34**,

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[14] diRienzo, F.; Domenicano, A.; Serantoni, E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 3854–3858.

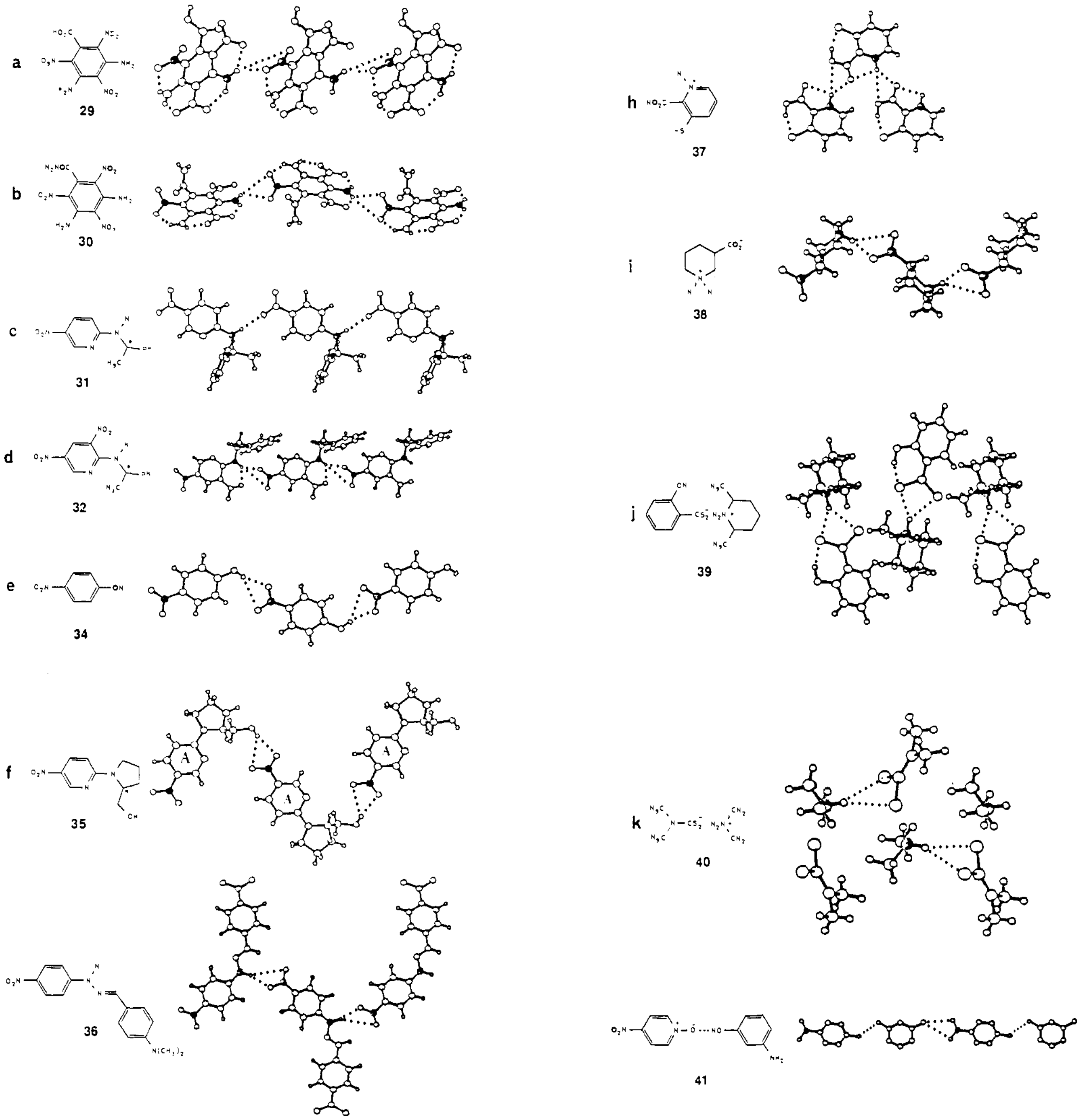

Figure 6. Polar hydrogen-bonded chain structures of nitroaniline analogues. The structures of compounds **29**, **30**, and **41** show that expected nitroaniline hydrogen-bond patterns can occur in the presence of other strong hydrogen-bonding groups. For *p*-nitrophenol, only the *β* polymorph (**34**) is shown (**33**, the *α* polymorph is nearly identical with *β*).

and **36**–**38** (Table II) are considerably shorter than the nitro–amino hydrogen bonds, as expected for the more acidic phenolic and more basic carboxylate groups. The dithiocarboxylate N···S distances (39, **40**) are longer than N···O distances because of the larger van der Waals radius of sulfur.

Compound **41** is an example of a mixed crystal that also follows the normal nitroaniline hydrogen-bond patterns. The strongest donor and acceptor in the two molecules of the complex are the phenol hydrogen and the nitroxide oxygen. These two groups form mixed dimers with strong intermolecular hydrogen bonds. The dimers associate through three-center bonds between the aniline and nitro groups on neighboring molecules to form polar chains (Figure 6). The dimer has meta-oriented nitro and amino groups, and it packs in an acentric and polar space group just as *m*-nitroaniline does. Compound **41** should be a good candidate for second harmonic generation.

Nitro Group Geometry. For the 52 nitro groups present in the compounds listed in Table I, the average N–O bond length is 1.22 Å, and the average ONO angle is 120.1°. The value of the ONO angle is about 6° smaller than that reported for aromatic nitro structures in the crystallographic literature before 1976.[15] From our data set of nitroaniline compounds, those nitro groups that participate in hydrogen bonding (44 nitro groups) have N–O bond lengths averaging 1.23 Å and ONO angles averaging 118.9°, while those that are "free" (8 nitro groups) have average N–O bond lengths equal to 1.21 Å and average ONO angles equal to 126.2°. The latter ONO value agrees with that of Holden,[15] since his set of structures contained predominantly free nitro groups. The smaller value of this angle for hydrogen-bonded nitro groups is confirming evidence that the N(H)···O interactions are three-centered and that both oxygens are attracted to the central proton. The smaller ONO bond angles could not be correlated with conjugative effects.

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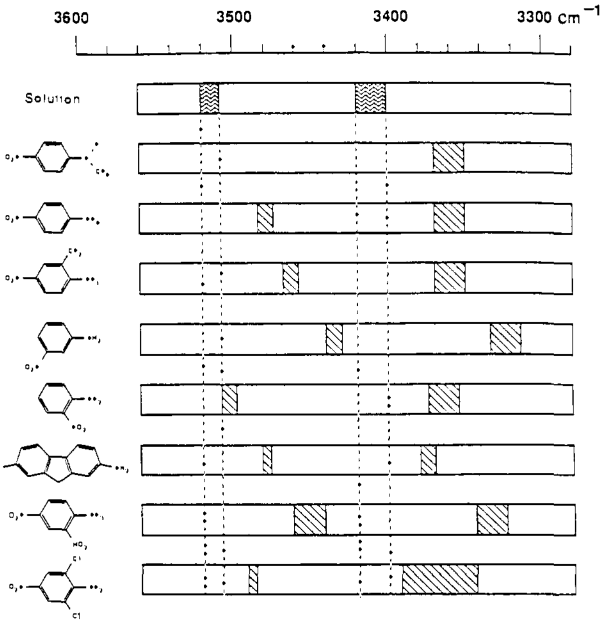
(15) Holden, J. R.; Dickinson, C. *J. Phys. Chem.* **1977**, *81*, 1505–1514.

Chart I. Positions of the N–H Stretching Frequencies for Selected Nitroanilines (Taken from IR Spectra)[a]



[a] The top spectrum is that of a 0.03 M solution of any of the nitroanilines. The others are spectra of solid-state Nujol mulls. The width of the shaded regions represents the actual bandwidth observed in the spectra.

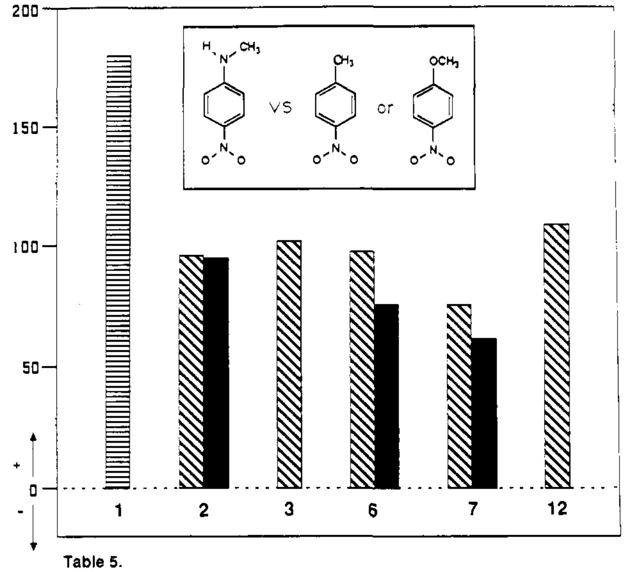
Hydrogen-Bond Strengths. The question of whether the NH···O contacts in nitroaniline structures are hydrogen bonds cannot be determined from geometrical data alone. If only van der Waals criteria are used, then an N···O contact longer than about 3.1 Å or (N)–H···O contact longer than 2.5 Å would not be considered a hydrogen bond.[13] Our scatterplots, however, show clear orientational preferences for association of amino groups and nitro groups even for some contacts that exceed these distances. In order to determine whether there is an energetic basis for classifying such long contacts as hydrogen bonds, we obtained spectroscopic and thermal data for the simplest nitroaniline structures.

IR spectra of compounds **1–3**, **6**, **7**, **10**, **12**, and **28** were run, and comparisons were made between the frequencies of the NH stretching bands in solution ($CHCl_3$) and in the solid state. For the primary amines, NH symmetric and asymmetric stretching frequencies are nearly invariant: $\nu_{as} = 3510 \pm 10$ and $\nu_s = 3410 \pm 10$ cm^{-1}. For secondary amines, a single NH solution frequency is observed at $\nu = 3450$ cm^{-1}. The observed positions of the solid-state NH stretching frequencies are given in Chart I.

In the solid state, all primary amines have two NH bands, and in some cases a third band occurs at lower frequency due to Fermi resonance.[16] The positions of the NH bands and their separation vary from compound to compound. Since all the compounds have the same IR absorption frequencies in solution, the solid-state differences must be caused by solid-state effects and not by differences in molecular structure. Since the NH_2 group is a coupled oscillator, changes in the force constant of one NH bond will affect the positions and intensities of both NH absorptions.[17] Comparison of solid-state frequencies with solution frequencies, $\Delta\nu$(solution–solid), reflects both coupling changes and shifts due to solid-state hydrogen bond interactions. Thus, $\Delta\nu$ will not be directly proportional to hydrogen bond strength.

A useful indicator of the presence of hydrogen bonds was found by comparing the average of the two solid-state NH frequencies with the average solution frequency. By this measure, the solid-state samples all showed bathochromic shifts of 20–90 cm^{-1} relative to solution frequencies. The magnitude of these shifts is comparable with that reported for solvent shifts of aniline NH bonds in strongly hydrogen-bonding solvents such as acetone[18] but is less than that for hydrogen bonds between hydroxyl and nitro groups.[19]

Chart II. Melting Point Differences between Selected Nitroanilines and Their Non-amino Analogues[a]

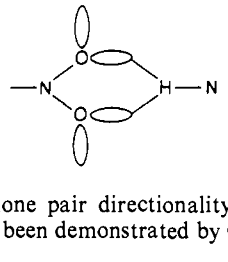


[a] The number of the parent aniline compound is given at the base of the chart. The bars correspond to the melting point difference (ΔT, °C) between the parent aniline and either its molecular weight analogue, where NH_2 has been replaced by CH_3 ▧ or CH_2CH_3 ▤ or by its electronic analogue where NH_2 has been replaced by OCH_3 ■. In all cases the melting point of the nitroaniline is higher than its analogues that have no hydrogen bonds.

The melting points of compounds **1–3**, **6**, **7**, and **12** listed in Chart II are compared with the melting points of compounds that are structurally analogous to the nitroanilines but that have no hydrogen bonds. A compound with a methyl group in place of an amino group has nearly the same molecular weight and size as the parent nitroaniline compound, while one with a methoxy group in place of an amino group has about the same dipole moment. Differences in melting points between these compounds and their aniline analogues are due mainly to hydrogen-bond effects. We found that compounds with amino protons melt 60–180 °C higher than the analogous compounds without amino protons or hydrogen bonds.

Discussion

NH···O Hydrogen Bonds in Nitroaniline Structures. Amine protons in nitroanilines were found to form intermolecular hydrogen bonds to nitro groups in all but two structures (**14**, **18**). The hydrogen bonds usually result in three-center interactions between an aniline proton and the two inside lone pairs of electrons of the nitro group on a neighboring molecule. The preferred geometry shows that the directionality of the nitro lone pairs of electrons is controlling the orientation of neighboring molecules.



The importance of lone pair directionality in hydrogen-bond patterns has recently been demonstrated by Glusker[20] and Dun-

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itz.[21] Our study was done in part to determine whether or not hydrogen bonds did form between these nitro groups and amino groups in nitroanilines. The recurring patterns of oriented nitro and amino groups give the strongest evidence that hydrogen-bonding interactions between nitro and amino groups are taking place, even when the interactions are longer than van der Waals distances.

The distribution of bond lengths and angles for these interactions is shown in bar charts in Chart IIIa–d. The N···O bond lengths cluster around 2.9–3.1 Å, and H···O lengths are 2.2–2.4 Å. The hydrogen bond angles, (N)—H···O, are 120–150°, and N=O···H angles are 100–120°. The aniline protons approach the nitro groups in the plane of the nitro group, so *D*, the distance of the protons from that plane, is rarely greater than 1 Å and is often less than 0.5 Å (Chart IIIe).

The values found here are consistent with the results reported from a statistical analysis of over 1500 NH···O=C hydrogen bonds.[22] Our N···O distances are in the same range as, but our H···O distances are longer than, those for the reported amide interactions. Taylor and Kennard's H···O values range from 2.002 (12) Å for carboxyl oxygens to 1.928 (19) Å for carboxylate oxygens. Since they reported corrected hydrogen atom positions, our values should be reduced by about 0.1 Å for comparison with theirs.[11] The NH···ONO hydrogen bond is consistently longer than NH···O=C hydrogen bonds. We include in Chart IIIb some H···O interactions that are even longer than van der Waals contacts, since those interactions give the same type of packing pattern as the other nitroaniline structures.

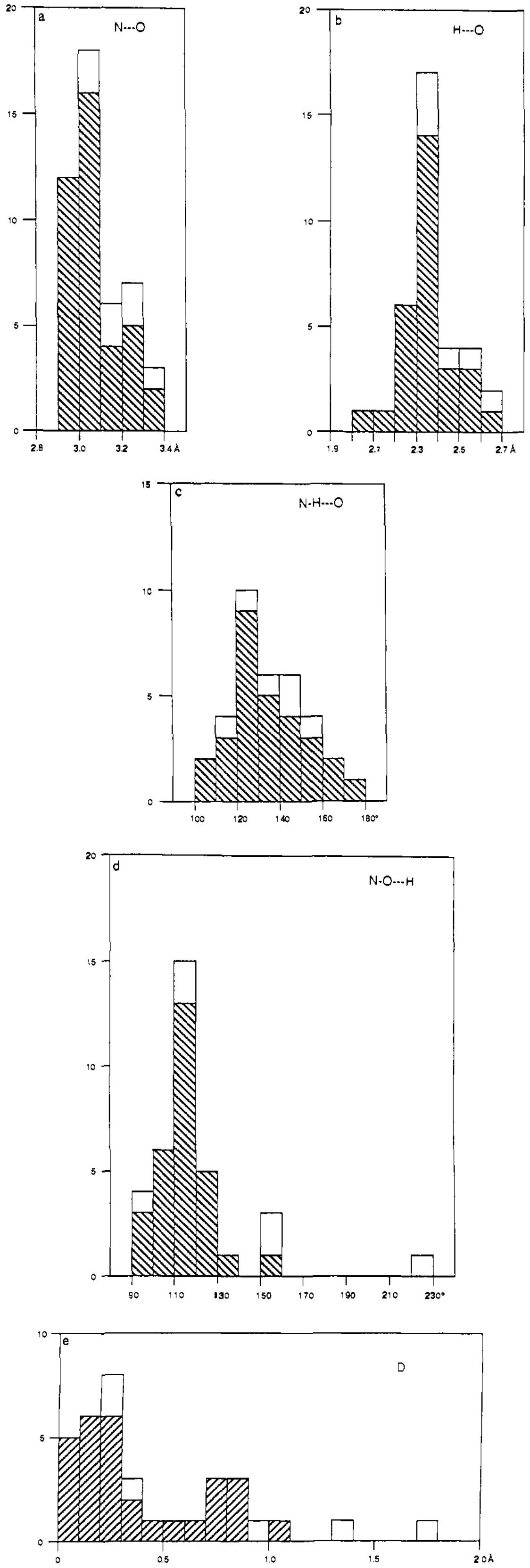
In order to form a three-center bond to a nitro group, the (N)–H···O angle must be considerably distorted from linearity, since the relative positions of the two acceptor oxygen atoms are fixed. This situation differs from that for amides, where a three-center intermolecular interaction usually involves three independent molecules.[22] The large distortions from linearity, apparent from the bar graph of (N)–H···O angles (Chart IIIc), are strong evidence that the bonds are truly three-centered and that even the long (N)–H···O contacts are stabilizing interactions.

There are two situations where a nitroaniline three-center bond is unlikely to form. First, when a primary amino group donates one of its protons to a three-center inside hydrogen bond, its second proton will form a two-center bond to a neighboring chain or to an intramolecular acceptor. Second, sterically overcrowded secondary amines sometimes form two-center bonds (**11**, **31**). In these compounds the N–O···HN angles are greater than 135°. Four-center bonds have also been found in some of our structures (**12**, **13**, **15**, **16**, **20–30**, **32**, **37**), but they always involve an intramolecular interaction as well as an intermolecular contact.

The hydrogen-bond data we have used comes from aromatic nitro acceptors and aromatic amine donors in nitroaniline derivatives. In these compounds mutual substituent effects should make the amine a better proton donor and the nitro group a better proton acceptor than in other aromatic or aliphatic nitro or amino compounds. The substituent effects also cause the nitrogen of the aniline function to be an "ineffective" acceptor. It is well-known that aniline groups can act as both proton donors and acceptors.[23] In nitroanilines, however, the amine nitrogen does not usually compete effectively with nitro groups for the amine protons. Only one nitroaniline in Table I (**17**) has an –NH···NH hydrogen bond. Other chemical effects such as loss of conjugation by substituents twisting out of the aromatic planes, electronic effects of other substituents on the ring, and molecular overcrowding are expected to mediate the proton-donating and -accepting properties of nitroanilines.

Predicting Hydrogen-Bond Patterns of Nitroanilines. Long H···O hydrogen bonds and small solid-state infrared frequency

Chart III. Distribution of (a) N···O (Å), (b) H···O (Å), (c) N-H···O (Deg), (d) N-O···H (Deg), and (e) *D* (Å) Found for the Primary (shaded), and Secondary (white), Amino–Nitro Contacts of Compounds Listed in Table I[a]



[a] N···O and H···O correspond to the shortest contact between the amino nitrogen or amino hydrogen and one of the nitro oxygens. N–H···O and N–O···H correspond to the angles made by these contacts. *D* denotes the distance of the amino hydrogen atom from the nitro plane (measured along a normal from the nitro plane to the hydrogen atom).

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shifts indicate that the NH···O interactions described here are weak interactions in comparison with amide bonds. Cooperative effects arising from the conjugated nature of the hydrogen-bonded chains may contribute an additional stabilizing force to these chains.[24] Nevertheless, the most important factor that determines these packing patterns is not the strength of the hydrogen bonds but their ability to organize molecules into aggregates. The strength of the hydrogen bond contributes to the stability of the crystals but does not influence the aggregate pattern of hydrogen-bonded molecules. Our analyses suggest that the orienting process precedes crystal nucleation and that polar aggregates formed in solution are preserved throughout the crystal growth process.

The use of the NH···ONO interaction for predicting crystal packing modes is derived primarily from the statistical distribution of hydrogen-bond geometries of known nitroaniline structures. The role of steric hindrance, conjugation, dipolar interactions, and solvent effects are implicit in the data, but further analyses are needed before these specific factors can be used as reliable predictors.

Listed below are features common to the crystal structures of compounds in Tables I and II that can be used as synthetic guidelines for preparing new solid-state structures based on nitroanilines.

1. All amino protons will form close contacts with nitro groups. These contacts may be intra- or intermolecular.
2. At least one intermolecular NH···O hydrogen bond should form.
3. The geometry of most NH···O hydrogen-bond patterns will be that of an inside three-center interaction.
4. Polar chain structures will form when nitro and amino groups are meta or para to one another.
5. Centric dimers may form when nitro and amino groups are ortho to one another.
6. Points 1–5 are valid even when strongly hydrogen-bonding functional groups such as carboxylic acids and amides are present in a nitroaniline compound.

The structures of compounds **33**–**40**, which are isographic with nitroanilines, show that hydrogen-bond rules developed for nitroanilines can be used to analyze and predict hydrogen-bond patterns of related compounds.

For nonlinear optical applications, one would like to design crystal structures that have predictable molecular orientations and that do not have inversion centers. The work presented here has shown how hydrogen bonds can be used to form acentric polymeric chains of molecules. Often these chains will pack about proper symmetry elements or glide planes to give acentric crystals. The challenge remains to find a way to control the packing patterns of these chains by molecular design or by crystal growth methods.

Acknowledgment. We thank the Office of Naval Research and the Naval Research Laboratory for financial support and Du Pont for a fellowship to T.W.P. We acknowledge Dr. R. J. Twieg, IBM Corp., for unpublished data on compounds **4**, **31**, **32**, and **35** and for helpful dicussions about this work. We also acknowledge Dr. R. Gilardi, Naval Research Laboratory, for background information about nitroamines and Dr. R. M. Joyce, Hockessin, DE, for editorial suggestions.

Registry No. 1, 100-15-2; **2**, 100-01-6; **3**, 99-52-5; **6**, 99-09-2; **7**, 88-74-4; **10**, 1214-32-0; **12**, 97-02-9; **28**, 99-30-9.

Supplementary Material Available: Cambridge Crystallographic Data Base search for nitroaniline analogues and tables of temperature factors, inter- and intramolecular bond lengths, and angles and esd's for *N*-methyl-*p*-nitroaniline (**1**) (35 pages); table of observed and calculated structure factors for **1** (3 pages). Ordering information is given on any current masthead page.

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Mesomorphic State of Cyclotetradecane

H. Drotloff,[†] **H. Rotter,**[‡] **D. Emeis,**[†,§] **and M. Möller***[†]

Contribution from the Institut für Makromolekulare Chemie and the Institut für Anorganische und Analytische Chemie, Universität Freiburg, D-7800 Freiburg, Federal Republic of Germany.
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Abstract: Cyclotetradecane shows a thermal transition 7 K below the melting point. The high-temperature crystal phase is characterized by high molecular mobility and easy deformation. Thermal analysis, MAS ^{13}C NMR with high-power proton decoupling, X-ray diffraction, and birefringence experiments have been performed and are discussed with respect to the onset of molecular motion and molecular disorder. The NMR experiments clearly show the onset of a conformational interconversion process well below the transition, while the positional, orientational, and conformational order are largely preserved. The same applies to some extent even within the high-temperature crystal phase. It is thus shown that molecular dynamics must be strictly differentiated from molecular and crystal disorder. Disordering of molecules with low symmetry such as cyclotetradecane is shown to result in rather large transition entropies, even when the molecular motions are jumplike and involve only minor disorder in the crystal. The concepts of liquid crystal, plastic crystal, and condis-crystal are discussed with regard to the classification of the mesomorphic character of the high-temperature crystal phase of cyclotetradecane. It is classified as a molecule that shows a mesophase with partial orientational disorder and high conformational mobility.

Many nonpolar, flexible-chain molecules undergo transitions from the fully ordered crystal to a phase of intermediate order and mobility. These include *n*-alkanes,[1] cycloalkanes,[2] poly(ethylene),[3] *trans*-1,4-poly(butadiene),[4] poly(tetrafluoroethylene),[5] poly(diethylsiloxane),[6] poly(*p*-xylylene),[7] and the polyphosphazenes.[8] In contrast to plastic crystals, these molecules

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[†] Institut für Makromolekulare Chemie.
[‡] Institut für Anorganische und Analytische Chemie.
[§] Present address: Beiersdorf AG, Hamburg.

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