remains basically unaltered in the context of different protection groups or in different environments. This can be concluded from the recently determined structure of Z-(Aib)$_7$-OMe (Pavone, Di Blasio, Pedone, Santini, Benedetti, Formaggio, Crisma & Toniolo, 1991). Despite very different crystalline environments, hydrations and differences in the orientation of the protection groups, the parameters of the helical parts of Z(Aib)$_7$-O'Bu and Z-(Aib)$_7$-OMe are in excellent agreement, with average deviations of only 4–5° in the conformational angles φ, ψ, and of 0.08 Å in the hydrogen-bond lengths.

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References

ARNOTT, S. & WONACOTT, A. J. (1966). *J. Mol. Biol.* **21**, 371–383.

BAKER, E. N. & HUBBARD, R. E. (1984). *Prog. Biophys. Mol. Biol.* **44**, 97–179.

BARLOW, D. J. & THORNTON, J. M. (1988). *J. Mol. Biol.* **201**, 601–619.

BAVOSO, A., BENEDETTI, E., DI BLASIO, B., PAVONE, V., PEDONE, C., TONIOLO, C. & BONORA, G. M. (1986). *Proc. Natl Acad. Sci. USA*, **83**, 1988–1992.

BLUNDELL, T., BARLOW, D., BORKAKOTI, N. & THORNTON, J. (1983). *Nature (London)*, **306**, 281–283.

BOSCH, R., JUNG, G., SCHMITT, H. & WINTER, W. (1985). *Acta Cryst.* C**41**, 1821–1825.

BRUECKNER, H. (1989). *Chemistry of Peptides and Proteins*, Vol. 4, edited by W. A. KOENIG and W. VOELTER, pp. 79–86. Tuebingen: Attempto Verlag.

BRUECKNER, H. & JUNG, G. (1982). *Liebigs Ann. Chem.* pp. 1677–1699.

DEBAERDEMAEKER, T., GERMAIN, G., MAIN, P., TATE, C. & WOOLFSON, M. M. (1987). *MULTAN*87. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

DEGRADO, W. F. (1988). *Adv. Protein Chem.* **40**, 51–124.

FOX, R. O. & RICHARDS, F. M. (1982). *Nature (London)*, **300**, 325–330.

GESSMANN, R., BRUECKNER, H. & KOKKINIDIS, M. (1991). *Biochem. Biophys. Res. Commun.* **174**, 878–884.

HOL, W. G., HALIE, L. M. & SANDER, C. (1981). *Nature (London)*, **294**, 532–536.

IUPAC–IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1970). *J. Mol. Biol.* **52**, 230–232.

JONES, D. S., KENNER, G. W., PRESTON, J. & SHEPPARD, J. (1965). *J. Chem. Soc.* p. 6227.

KARLE, I. L., FLIPPEN-ANDERSON, J. L., UMA, K. & BALARAM, P. (1990). *Proteins*, **7**, 62–73.

KOKKINIDIS, M., BANNER, D. W., TSERNOGLOU, D. & BRUECKNER, H. (1986). *Biochem. Biophys. Res. Commun.* **139**, 590–595.

KOKKINIDIS, M., TSERNOGLOU, D. & BRUECKNER, H. (1986). *Biochem. Biophys. Res. Commun.* **136**, 870–875.

MOTHERWELL, W. D. S. & CLEGG, W. (1987). *PLUTO*. Program for plotting molecular and crystal strucutures. Univ. of Cambridge, England.

NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.

PATERSON, Y., RUMSEY, S. M., BENEDETTI, E., NEMETHY, G. & SHERAGA, H. A. (1981). *J. Am. Chem. Soc.* **103**, 2947–2955.

PAVONE, V., DI BLASIO, B., PEDONE, C., SANTINI, A., BENEDETTI, E., FORMAGGIO, A., CRISMA, M. & TONIOLO, C. (1991). *Gazz. Chim. Ital.* **121**, 21–27.

ROBERTS, P. & SHELDRICK, G. M. (1985). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.

SCHMITT, H., WINTER, W., BOSCH, R. & JUNG, G. (1982). *Liebigs Ann. Chem.* pp. 1304–1321.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1986). *SHELXS*86. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

VLASSI, M., BRUECKNER, H. & KOKKINIDIS, M. (1992). *Z. Kristallogr.* **202**, 89–98.

Acta Cryst. (1993). B**49**, 564–576

Resonance-Assisted Hydrogen Bonding. III. Formation of Intermolecular Hydrogen-Bonded Chains in Crystals of β-Diketone Enols and its Relevance to Molecular Association*

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Abstract

The β-diketone enol (or enolone) HO—C=C—C=O fragment produced by enolization of β-diketones is known to form strong intramolecular O—H···O hydrogen bonds where the decrease of the O···O contact distance (up to 2.40 Å) is correlated with the increased π-delocalization of the O—C=C—C=O heteroconjugated system; the phenomenon has been interpreted by the resonance-assisted hydrogen-bonding (RAHB) model [Gilli,

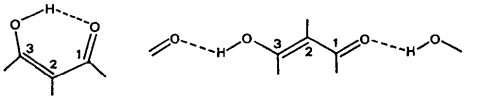
* The previous two papers of this series have been published as: I (Gilli, Bellucci, Ferretti & Bertolasi, 1989) and II (Bertolasi, Gilli, Ferretti & Gilli, 1991).

0108-7681/93/030564-13$06.00

Bellucci, Ferretti & Bertolasi (1989). *J. Am. Chem. Soc.* **111**, 1023–1028; Bertolasi, Gilli, Ferretti & Gilli (1991). *J. Am. Chem. Soc.* **113**, 4917–4925]. When the intramolecular hydrogen bond is forbidden for steric reasons, molecules crystallize by forming hydrogen-bonded infinite chains of π-delocalized enolone fragments (*resonant β-chains*), *i.e.* they are hybrids of the canonical forms —OH···O=C—C= C—OH···O=C— $\leftrightarrow$ $=^{+}$OH···$^{-}$O—C=C—C= $^{+}$OH···$^{-}$O—C=. The occurrence of β-chains in 14 crystals of enolone (2-en-3-ol-1-one) and eight of enediolone (2-en-2,3-diol-1-one) derivatives has been studied. The β-chains were found to have the following properties: (i) O···O distances depend on the enediolone substituents and range from 2.69 Å in β-ketoesters to 2.46 Å in β-diketones; (ii) calculated hydrogen-bond energies are in the range 20–66 kJ mol^{-1}; (iii) a strict intercorrelation between hydrogen-bond strengthening and π-system delocalization is observed, in complete agreement with the RAHB model proposed previously. β-Chain morphologies are analyzed with the aim of determining crystal-engineering rules for the production of solid materials where systems of polar β-chains can induce ferroelectric and second harmonic generation properties. The RAHB concept is generalized to other heteroconjugated systems such as carboxylic acids, amides, enamines (*R*N=C*R*—NH*R*) and enaminones (O=C*R*—C*R*=C*R*—NH*R*), and its possible relevance in biological processes such as base coupling in DNA and folding of proteins is briefly discussed.

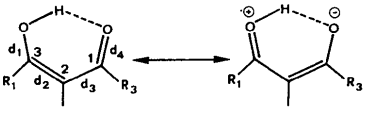
Introduction

Recent papers (Gilli, Bellucci, Ferretti & Bertolasi, 1989; Gilli & Bertolasi, 1990) have shown that intramolecular (I*a*) and intermolecular (I*b*) hydrogen bonds formed by β-diketone enols (or enolones) display specific features: (i) the O···O distance may become as short as 2.40–2.42 Å for the intramolecular (Emsley, Ma, Bates, Motevalli & Hursthouse, 1989; Görbitz, Mostad, Pedersen, Rasmussen & Lawesson, 1986; Jones & Power, 1976; Norrestam, von Glehn & Wachtmeister, 1974) and 2.46–2.48 Å for the intermolecular case (Bideau, Bravic & Filhol, 1977; Gavuzzo, Mazza, Carotti & Casini, 1984), at variance with polyalcohols and saccharides having average d(O···O) values of 2.77 (7) Å (Kroon, Kanters, Van Duijneveldt-Van de Rijdt, Van Duijneveldt & Vliegenthart, 1975; Ceccarelli, Jeffrey & Taylor, 1981); (ii) the d(O···O) shortening is associated with a remarkable increase of delocalization in the O=C—C=C—OH π-conjugated system; and (iii) it is paralleled by changes of d(O—H) from 0.97 up to 1.20 Å (Bertolasi, Gilli, Ferretti & Gilli, 1991), of IR ν(OH) stretching frequencies from 3600 to 2500 cm^{-1} and of ^{1}H NMR chemical shifts of the enolic proton from some 5–8 to 17 p.p.m., while the difference between C_1 and C_3 chemical shifts in ^{13}C CP/MAS solid-state NMR tends to vanish (Emsley, 1984; Floris, 1990; Novak, 1974; Etter & Vojta, 1989; Etter, Hoye & Vojta, 1988). At the same time hydrogen-bond energies, evaluated from spectroscopic (Kopteva & Shigorin, 1974), empirical (Lippincott & Schroeder, 1955; Schroeder & Lippincott, 1957) or theoretical (Frisch, Scheiner, Schaefer & Binkley, 1985) methods, may become three times greater than the accepted value for the O—H···O bond in water (*ca* 17–21 kJ mol^{-1}) (Pimentel & McClellan, 1960, 1971).



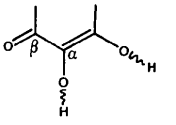
(I*a*) (I*b*)

Such phenomena have been interpreted by recognizing that the π-system delocalization (II*a*) $\leftrightarrow$ (II*b*) gives rise to partial charges on the opposite O atoms which have the correct signs for shortening the O···O and lengthening the O—H distances, thus triggering a synergistic mechanism between hydrogen-bond strengthening and resonance reinforcement which has been called *resonance-assisted hydrogen bonding* (RAHB) (Gilli *et al.*, 1989).



(II*a*) (II*b*)

Recently published results (Bertolasi *et al.*, 1991; Gilli, Ferretti, Bertolasi & Gilli, 1992) on nine 1,3-diaryl-1,3-propanedione enols forming strong intramolecular O—H···O hydrogen bonds have shown that both crystal and spectroscopic data are in agreement with the RAHB model. The present paper deals with the role played by RAHB in strengthening the intermolecular, instead of the intramolecular, hydrogen bond in molecular crystals of enolone [(I*b*) 2-en-3-ol-1-one] or enediolone [(III) 2-en-2,3-diol-1-one] derivatives.



(III)

Other aspects of this research concern the self-association properties of β-diketone enol fragments

Table 1. *Intermolecular hydrogen-bonded structures and selected data for 2-en-3-ol-1-one derivatives*

(*a*) Intermolecular hydrogen-bonded structures

SG = space group; Z = number of asymmetric units in the space group; symmetry operations: t = translation, g = glide, 2_1 = 2_1 screw axis, i = center, A–B, C–D = asymmetric unit built up of two molecular units.

No.	Refcode	SG	Z	Chain type	Chain symmetry	Chain conformation	Notes	Ref.
(1)	PROLON	$Pna2_1$	4	β	g	*ap-anti-ANTI*		(*a*)
(2)	FACRIK	$P2_1/a$	4	β	g	*ap-anti-ANTI*		(*b*)
(3)	FIVKEA	$P2_1$	4	β	$t(A$–$B)$	*ac-anti-ANTI*	Polar chain Chiral molecule	(*c*)
(4)	DETSBR01	$P2_12_12_1$	4	β	2_1	*ap-syn-SYN*		(*d*)
(5)	FERBUZ	$C2/c$	8	β	2_1	*sp-syn-SYN*		(*e*)
(6)	DIMEDO	$P2_1/c$	4	β	2_1	*sc-syn-SYN*		(*f*)
(7)	BOMYAD01	$P2_1/c$	8	β	$t(A$–$B)$ (pseudo 2_1)	*sc-syn-SYN*		(*g*)
(8)	CIHNAI	$Pca2_1$	4	β	2_1	*sc-syn-SYN*	Polar chain	(*h*)
(9)	BEWHUG	$P2_1$	2	β	t	*ap-syn-ANTI*	Polar chain Chiral molecule	(*i*)
(10)	FACROQ	$R\bar{3}$	18	β	$(6/m)$	*ap-syn-ANTI*	6-Membered ring	(*j*)
(11)	MTETAC02	$P2_1/c$	4	β	t	*ap-anti-SYN*		(*k*)
(12)	DMTETA01	$P2_1/c$	4	β	t	*ap-anti-SYN*		(*l*)
(13)	SEFSIF	$C2/m$	4	β	t	*ap-anti-SYN*		(*m*)
(14)	GANHUY	$P2_1/n$	16	β	$t(C$–$D)$	*ac-syn-ANTI-* *-ac-anti-SYN*		(*n*)
				β	$t(A$–$B)$	*ac-anti-SYN*		

(*b*) Selected data

Distances in Å, angles in ° and energies in kJ mol^{-1}; X = X-rays, N = neutrons, R = discrepancy index; for Q (in Å), λ and calculated energies E_{HB} see text; $\langle\ \rangle$ = average values; e.s.d.'s in parentheses.

No.	Refcode	(X/N)	T (K)	R	d(O···O)	δ(O—H···O)	Q	λ	E_{HB}	Notes
(1)	PROLON	X	111	0.032	2.577 (2)	175 (2)	0.135 (4)	0.71	34.7	
(2)	FACRIK	X	298	0.052	2.539 (3)	169 (5)	0.163 (6)	0.75	41.0	
(3)	FIVKEA	X	298	0.034	⟨2.609⟩ (5)	⟨167⟩ (2)	⟨0.204⟩ (10)	0.82	⟨28.4⟩	Thioester
(4)	DETSBR01	N	298	0.043	2.465 (5)	176 (5)	0.084 (10)	0.63	65.3	Barbituric
(5)	FERBUZ	X	298	0.039	2.603 (2)	163 (2)	0.126 (4)	0.70	27.6	Barbituric
(6)	DIMEDO	X	298	0.046	2.593 (2)	176 (2)	0.147 (4)	0.73	32.2	
(7)	BOMYAD01	X	120	0.059	⟨2.588⟩ (3)	⟨172⟩ (2)	⟨0.136⟩ (6)	0.71	⟨31.0⟩	
(8)	CIHNAI	X	298	0.058	2.477 (5)	169 (5)	0.036 (10)	0.56	57.7	Pyrazolone
(9)	BEWHUG	X	133	0.048	2.685 (5)	159 (5)	0.217 (10)	0.84	16.7	Ester
(10)	FACROQ	X	298	0.037	2.579 (2)	174 (2)	0.127 (4)	0.70	34.3	
(11)	MTETAC02	X	298	0.050	2.601 (3)	151 (4)	0.202 (6)	0.82	23.0	Ester
(12)	DMTETA01	X	295	0.039	2.629 (2)	178 (2)	0.213 (4)	0.83	26.8	Ester
(13)	SEFSIF	X	298	0.040	2.598 (2)	174 (2)	0.164 (4)	0.76	31.0	
(14)	GANHUY	X	133	0.038	⟨2.543⟩ (4)	⟨172⟩ (4)	⟨0.127⟩ (8)	0.70	⟨31.0⟩	

Chemical names: (1) phenylmalondialdehyde; (2) 1,3-cyclohexanedione; (3) (5*R*)-2,5-dihydro-4-hydroxy-5-methyl-3-phenyl-5-prop-1′-enyl-2-oxothiophene; (4) 1,3-diethyl-2-thiobarbituric acid; (5) 5-phenylbarbituric acid; (6) 5,5-dimethyl-1,3-cyclohexanedione (dimedone); (7) 4-hydroxybicyclo[3.3.1]non-3-en-2,9-dione; (8) 7-(5-hydroxy-3-oxo-2,3-dihydro-4-pyrazolyl)theophilline; (9) (−)-4-hydroxy-3,5-dimethyl-5-[3-oxo-(*E*,*E*)-4,6-octadienyl]-2(5*H*)-furanone (vertinolide); (10) 6:1 1,3-cyclohexanedione:benzene cyclamer; (11) α-methyltetronic acid; (12) DL-α,γ-dimethyltetronic acid; (13) 2-methyl-1,3-cyclopentanedione; (14) 3-hydroxy-3-cyclobutene-1,2-dione (semisquaric acid).

References: (*a*) Semmingsen (1977*b*); (*b*) Etter, Urbanczyk-Lipkowska, Jahn & Frye (1986); (*c*) Chambers, Thomas & Williams (1987); (*d*) Bideau, Bravic & Filhol (1977); (*e*) de Meester, Jovanovich, Chu & Biehl (1986); (*f*) Semmingsen (1974*a*); (*g*) Schönwälder, Kollat, Stezowski & Effenberger (1984); (*h*) Gavuzzo, Mazza, Carotti & Casini (1984); (*i*) Trifonov, Bieri, Prewo, Dreiding, Rast & Hoesch (1982); (*j*) Etter *et al.* (1986); (*k*) Krogh Andersen & Krogh Andersen (1975); (*l*) Krogh Andersen, Krogh Andersen & Ploug-Sørensen (1987); (*m*) Katrusiak (1989); (*n*) Semmingsen & Groth (1988).

in relation to the fact that crystals containing infinite chains of such fragments are potential nonlinear dielectrics because of the β-diketone enol tautomerism and, accordingly, have aroused growing interest in the field of nonlinear optics (NLO), particularly as second harmonic generation (SHG) materials (Chemla & Zyss, 1987; Prasad & Williams, 1991).

Data retrieval and treatment

Crystallographic data were retrieved from the Cambridge Structural Database (Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1979) (November 1991 release); the CSD reference codes have been retained throughout the text. Only the X-ray or neutron structures having $R < 0.10$, σ(C—C) < 0.010, no disorder in the fragment of interest, and refined enolic H atoms were retained. When both an X-ray and a neutron structure was available, the latter was used.

Enolone fragment

A total of 45 structures were found. In 16 the enol group forms intramolecular hydrogen bonds with other functional groups casually present in the molecule and are not given consideration here. Out of the 29 structures of interest, 19 form hydrogen-bonded chains (I*b*) (hereafter called *β-chains*), while in the remaining ten the enol fragment is solvated by

different hydrogen-bond donors or acceptors (BF_4^-, Cl^-, $R—O^-$, $>C=O$, H_2O). The homonuclear β-chain is therefore preferred in 19/29 packing arrangements. For the sake of simplicity, only the 14 structures where the β-chain is not involved in further hydrogen bonds (*e.g.* with solvent molecules or other donor or acceptor groups of the same molecule) are illustrated here (Fig. 1) and their relevant data and references are summarized in Tables 1(*a*) and 1(*b*). However, data for the other five structures (Zvilichovsky, 1987; Schwalbe & Saenger, 1973; Alden, Stout, Kraut & High, 1964; Graves & Hodgson, 1981; Low & Wilson, 1983) are included in the scatterplot of Fig. 4.

Enediolone fragment

Only ten structures containing such a fragment were found, out of which eight form β-chains (in some cases in addition to other hydrogen bonds).

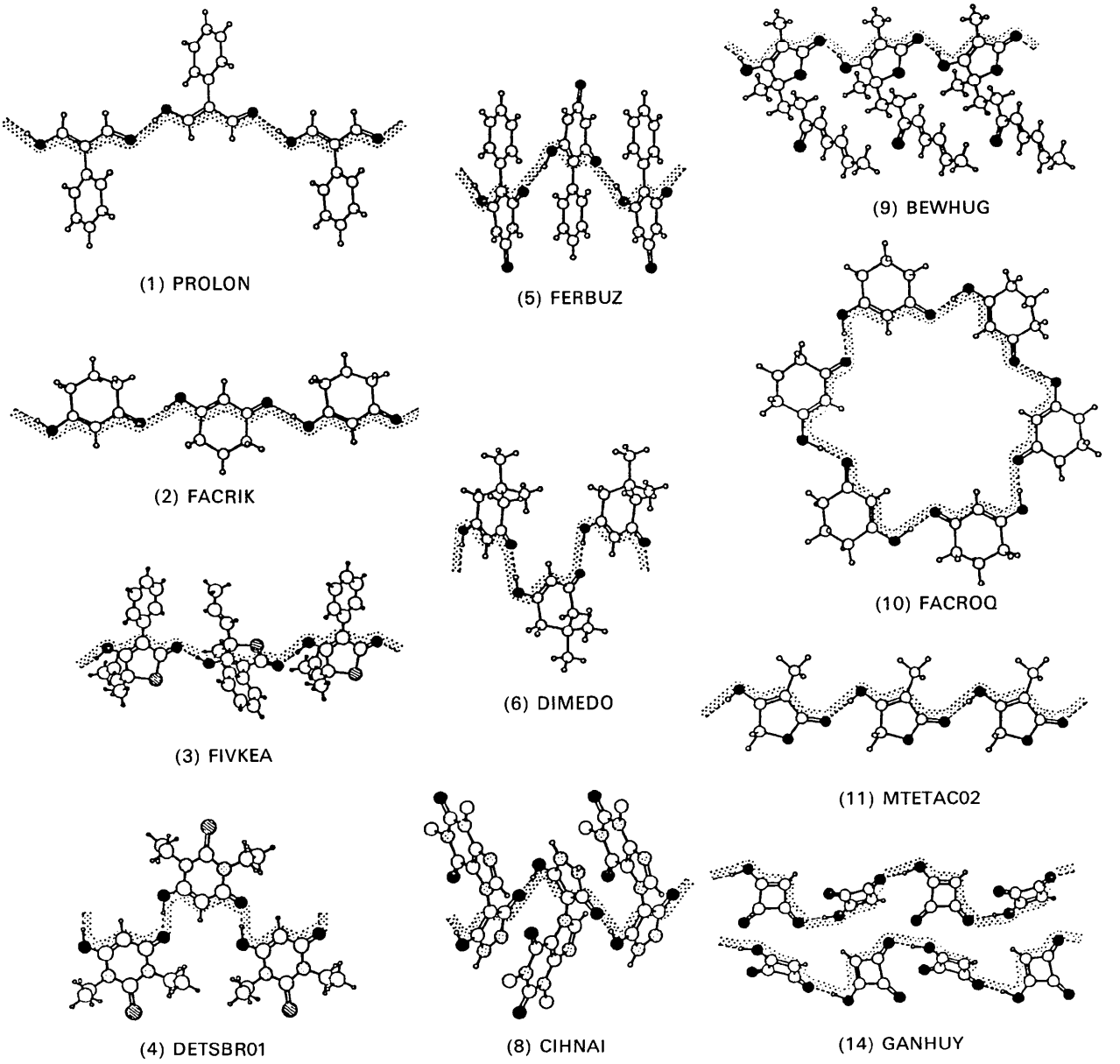
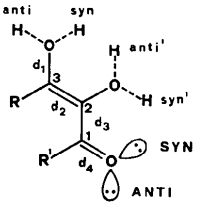


Fig. 1. Schemes of the hydrogen-bond interactions observed in the crystal packing of enolones of Table 1. The scheme for DIMEDO (6) is also representative of that for BOMYAD01 (7), and that for MTETAC02 (11) of those for DMTETA01 (12) and SEFSIF (13). The β-chains are marked by shading.

Relevant data for the eight structures considered (Fig. 2) are collected in Tables 2(*a*) and 2(*b*).

Several methods have been proposed for classifying the net of hydrogen bonds found in organic molecular crystals (Etter, Urbanczyk-Lipkowska, Jahn & Frye, 1986; Kuleshowa & Zorky, 1980; Etter, MacDonald & Bernstein, 1990; Etter, 1990). In this paper, the hydrogen-bonded chains are described by the use of two different schemes. The first is *crystallographic* and makes use of the symmetry operations relating subsequent molecules in the chain. The symbols *g* for glide, 2_1 for 2_1 screw axis and *t* for simple translation along the chain are used (Tables 1*a* and 2*a*). Multiple asymmetric units are indicated as *A–B* (or *C–D*), so that the notation *t*(*A–B*) indicates an asymmetric unit of two crystallographically independent interlinked molecules propagating the chain by simple translation. Approximate non-crystallographic symmetry elements are also reported, *e.g. pseudo* 2_1. The second type of classification is *stereochemical* and follows the (*syn/anti-SYN/ANTI*) nomenclature, (IV), proposed by Etter *et al.* (1986) for describing the conformations around the C_1—O_1 and C_3—O_3 bonds observed in β-diketone enols. To include the hydrogen bonds formed by α-hydroxyls, a further (*syn′/anti′*) specification has been added. The global β-chain conformation is also determined by the rotation around the intermolecular C—OH···O=C linkage, which has been measured by the values of the C—O···O—C torsion angle according to the Klyne & Prelog (1960) convention [*sp* = synperiplanar, *sc* = synclinal, *ac* = anticlinal, *ap* = antiperiplanar for torsion angles in the ranges ± 30, ± (30–90), ± (90–150) and 150–210°, respectively]. For the sake of clarity, chain structural types arising from (*syn/anti-SYN/ANTI*) differences will be hereafter called *C—O conformations* and those generated by variations of the C—O···O—C torsion angles *O···O conformations*.



(IV)

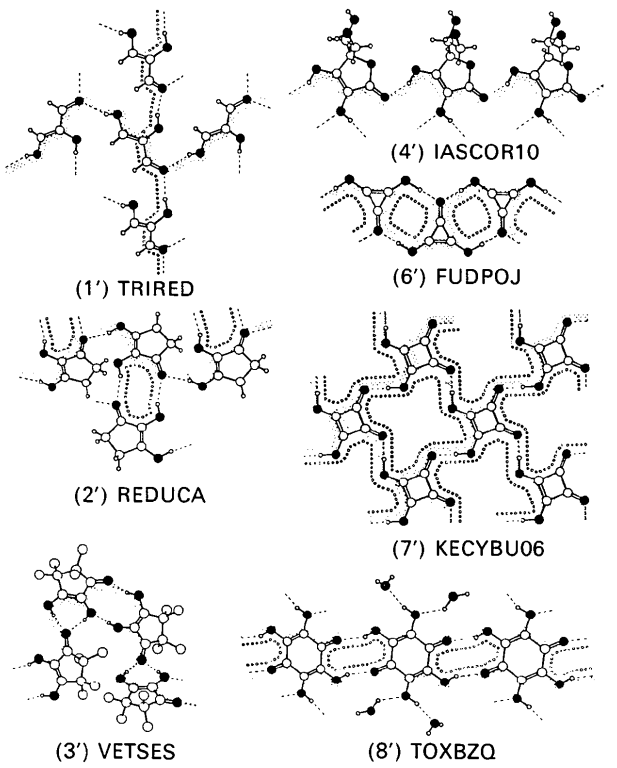


Fig. 2. Schemes of the hydrogen-bond interactions observed in the crystal packing of enediolones of Table 2. The scheme for IASCOR10 (4′) is also representative of that for LASCAC10 (5′). The β-chains are marked by darker or lighter shadings and α-chains or rings by lines of small open squares.

All fragments investigated display the *zigzag planar* structure (IV) and are essentially planar as far as the non-H atoms are concerned. Such a structure is mostly produced by fusion of *R* and *R′* substituents in a same ring.

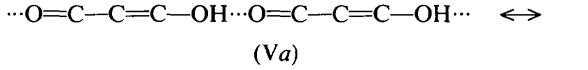
d(O···O) contact distances are natural geometrical indicators of the hydrogen-bond strength. The antisymmetrical stretching coordinate $Q = d_1 - d_4 + d_3 - d_2$ (II) can be used as an appropriate π-delocalization index; taking $d_1 = 1.37$, $d_2 = 1.33$, $d_3 = 1.48$ and $d_4 = 1.20$ Å for pure single- and double-bond lengths (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987), *Q* is calculated to assume the extreme values of + 0.320 Å for the totally π-localized keto-enol form (II*a*) and − 0.320 Å for its specular enol-keto form, while it will be zero for the intermediate totally π-delocalized system. The actual heterodiene geometry can be described also as a mixture of these two specular forms according to λ(enol-keto) + (1 − λ)(keto-enol), where λ is a coupling parameter related to *Q* by the equation $\lambda = (1 + Q/0.320)/2$. Values of *d*(O···O), *Q* and λ are given in Tables 1(*b*) and 2(*b*). O—H distances are not reported in view of the very small number of neutron investigations. In all X-ray studies, however, the hydroxylic proton was identified and refined, and found to be located on the side of the longer C—O bond of the enolone fragment (II); no case of static or dynamic proton disorder was observed. The δ(O—H···O) angles range from 151 to 178° and, of a total of 24 hydrogen bonds, ten have deviations from linearity of less than 10° and 17 of less than 20°.

Chain morphology

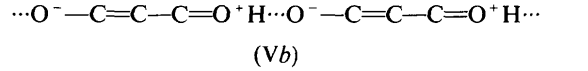
By analyzing the crystal packings of these compounds it is possible to identify the different hydrogen-bonded chain patterns which are shown in Figs. 1 and 2 for enolones and enediolones, respectively.

All enolones (Fig. 1) form infinite hydrogen-bonded β-chains with the exception of FACROQ (10) which contains six-membered rings of cyclohexanedione molecules surrounding a solvated benzene (not shown). In the absence of solvent, however, the same compound forms the more common β-chain of FACRIK (2), suggesting that the circular arrangement is not favoured in crystal nucleation or growth. The lower stability of the ring with respect to the β-chain is supported by the comparison of the d(O···O) distances, which are 2.579 (1) in FACROQ (10) and 2.539 (4) Å in FACRIK (2). A recent review (Gilli & Bertolasi, 1990) has shown that β-diketone enols form, whenever possible, the intramolecular hydrogen bond (I*a*), probably favoured by entropic factors (chelate effect); the predominance of β-chains in the present compounds is due to their inability to close intramolecular hydrogen bonds, being the enolone group part of a ring. PROLON (1) and TRIRED (1′) are the only known exceptions to this rule.

β-Chains have in common the linking end-to-tail of the 1,3-O atoms in infinite hydrogen-bonded chains where the π-conjugated heterodienic group is always more or less delocalized (see below), their ground state being representable as a mixture of the two extreme resonant forms (V*a*) and (V*b*). In this sense they might be named *resonant β-chains*.



(V*a*)



(V*b*)

The packing of enediolones (Fig. 2) is more complex because of the additional α-hydroxyl groups. For instance, in TRIRED (1′) β-chains are intersected by a second system of chains linking the non-conjugated 1,2-O atoms, which may be called *non-resonant α-chains* (in Figs. 1 and 2 β-chains are marked by darker or lighter shadings and α-chains or α-rings by lines of small open squares). α-Chains occur (independently of the β-chains) only in another case [reductic acid, REDUCA (2′)] in the form of α-rings connecting two antidromic β-chains. The predominance of β over α structures is a first indication that the hydrogen-bond stabilization energy is greater in resonant β-chains than in ordinary (non-resonant) O—H···O interactions.

The packings of deltic acid [FUDPOJ (6′)], squaric acid [KECYBU06 (7′)] and tetrahydroxy-*p*-benzoquinone [TOXBZQ (8′)] are more complex because the molecular symmetry makes it impossible to distinguish α and β hydroxyls. Yet, α and β structures remain identifiable as is shown in Fig. 2 and discussed in greater detail in a later section.

Since the presence of chains iso-oriented along a unique polar axis is a prerequisite for producing ferroelectric behaviour, the occurrence of such chains has been investigated. Of a total of 22 crystals, 14 belong to centrosymmetric space groups, one to the space group $P2_12_12_1$, which is not polar, three to space groups of the point group $mm2$ [out of which only one, CIHNAI (8), has β-chains oriented along the polar axis] and four to space group $P2_1$ [(3), (9), (4′) and (5′)]. Though the last four compounds are chiral, only FIVKEA (3) and BEWHUG (9) display polar chains, while in the others [(4′) and (5′)] pairs of antidromic β-chains are related by the 2_1 axis along **b**. In conclusion, there are only three cases of β-chains oriented along a unique polar axis over 22 structures. The difficulty in forming single polar chains appears to be due to dipolar interactions among the β-chains (see *Discussion and generalization*).

Tables 1(*a*) and 2(*a*) and Fig. 3 report the chain classification according to the two types of nomenclature already described. Molecules forming the chain can be related by simple cell translation t [chain types (*F*), (*G*), (*H*) and (*J*) in Fig. 3], by crystallographic glides g [(*A*), (*I*), (*K*)] or binary screw axes 2_1 [(*C*), (*D*)]. Some crystals are seen to repeat an asymmetric unit consisting of two molecules t(*A*–*B*) [(*B*), (*D*), (*E*), (*L*) and (*M*)], perhaps to allow a more energetically favourable matching between the two *A* and *B* subunits. Deviations from the crystallographic repetition may be small, as shown by (7) whose chains have a pseudo 2_1 arrangement [(*D*) of Fig. 3], or may be enhanced by the use of a greater number of subunits in the asymmetric unit, as in (14) [(*L*) and (*M*)], where four subunits are seen to form two different t(*A*–*B*) and t(*C*–*D*) chains.

β-Chains have only four possible C—O conformations, *i.e. anti-ANTI*, *syn-SYN*, *syn-ANTI* and *anti-SYN* (IV) and each of these can assume different O···O conformations according to the C—O···O—C torsion angle. Actually, *syn-ANTI* and *anti-SYN* conformations are equivalent by tautomerism, as shown by the comparison of the two *syn-ANTI* and *anti-SYN* chains (*F*) and (*G*) of Fig. 3.

Chain lengths are affected by both conformational degrees of freedom. The effect of C—O conformation can be seen in fully extended chains [*ap*: (*A*), (*C*), (*F*), (*G*), (*H*), (*J*)] whose measured lengths decrease in the order *anti-ANTI* > *syn-ANTI* = *anti-*

Table 2. *Intermolecular hydrogen-bonded structures and selected data for* 2-*en*-2,3-*diol*-1-*one derivatives*

(*a*) Intermolecular hydrogen-bonded structures

SG = space group; Z = number of asymmetric units in the space group; symmetry operations: t = translation, g = glide, 2_1 = 2_1 screw axis, i = center, A–B, C–D = asymmetric unit built up of two molecular units.

No.	Refcode	SG	Z	Chain type	Chain symmetry	Chain conformation	Notes	Ref.
(1′)	TRIRED	$Pna2_1$	4	β	g	*sc-anti-SYN*	Intercrossing	(*a*)
				α	g	*sp-anti′-ANTI*	α- and β-chain	
(2′)	REDUCA	$P2_1/c$	4	β	g	*sc-syn-ANTI*	β-Chains linked in	(*b*)
				α	*i*(dimer)	*sp-syn′-SYN*	pairs by α-dimers	
(3′)	VETSES	*Pbca*	16	β	$t(A–B)$	*ac-syn-SYN-*		(*c*)
						-sc-syn-SYN		
(4′)	IASCOR10	$P2_1$	2	β	t	*ap-syn-ANTI*	Chiral molecule	(*d*)
(5′)	LASCAC10	$P2_1$	4	β	$t(A–A)$	*ap-syn-ANTI*	Chiral molecule	(*e*)
					$t(B–B)$			
(6′)	FUDPOJ	*Pnam*	4	β	$i + t$	*sp-anti-SYN*	Two interlacing β-chains	(*f*)
(7′)	KECYBU06	$P2_1/m$	2	β	t	*ap-syn-ANTI*	Two intercrossing	(*g*)
				β	t	*ap-anti-SYN*	β-chains	
(8′)	TOXBZQ	$P2_1/c$	2	β	$i + t$	*sp-anti-ANTI*	Two antidromic β-chains	(*h*)

(*b*) Selected data

Distances in Å, angles in ° and energies in kJ mol^{-1}; X = X-rays, N = neutrons, R = discrepancy index; for Q (in Å), λ and calculated energies E_{HB} see text; ⟨ ⟩ = average values; e.s.d.'s in parentheses.

No.	Refcode	(*X*/*N*)	T (K)	R	d(O···O)	δ(O—H···O)	Q	λ	E_{HB}	Notes
(1′)	TRIRED	*X*	298	0.035	β: 2.635 (2)	156 (2)	0.143 (4)	0.72	20.1	
					α: 2.744 (2)	165 (2)	–		13.4	
(2′)	REDUCA	*X*	298	0.044	β: 2.647 (1)	163 (1)	0.149 (2)	0.73	22.2	
					α: 2.746 (1)	158 (1)	–		14.6	
(3′)	VETSES	*X*	298	0.051	⟨2.649⟩ (3)	⟨166⟩ (3)	⟨0.146⟩ (6)	0.73	⟨23.0⟩	
(4′)	IASCOR10	*X*	298	0.037	2.645 (5)	151 (5)	0.244 (10)	0.88	18.0	Ester
(5′)	LASCAC10	*N*	298	0.090	⟨2.661⟩ (3)	⟨153⟩ (3)	⟨0.224⟩ (6)	0.85	24.3	Ester
(6′)	FUDPOJ*	*X*	135	0.034	2.555 (1)	178 (1)	0.060 (2)	0.59	39.3	
(7′)	KECYBU06†	*N*	298	0.025	⟨2.553⟩ (1)	⟨177.6⟩ (1)	⟨0.108⟩ (2)	0.67	39.7	
(8′)	TOXBZQ	*X*	298	0.079	2.744 (5)	156 (5)	0.254 (10)	0.90	11.3	

Chemical names: (1′) 2,3-dihydroxy-2-propen-1-one (triose reductone); (2′) 2,3-dihydroxy-2-cyclopenten-1-one (reductic acid); (3′) 4,4,5,5-tetramethyl-2,3-dihydroxy-2-cyclopenten-1-one (tetramethylreductic acid); (4′) D-isoascorbic acid; (5′) L-(+)-ascorbic acid (vitamin C); (6′) 2,3-dihydroxycyclopropen-1-one (deltic acid); (7′) 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid); (8′) tetrahydroxy-*p*-benzoquinone.

References: (*a*) Semmingsen (1974*b*); (*b*) Semmingsen (1977*a*); (*c*) Feng, Bott & Lippard (1990); (*d*) Azarnia, Berman & Rosenstein (1971); (*e*) Hvoslef (1968); (*f*) Semmingsen & Groth (1987); (*g*) Semmingsen, Hollander & Koetzle (1977); (*h*) Klug (1965).

* d(C=O) = 1.265 (1), d(HOC=COH) = 1.397 (1), d(HOC—CO) = 1.397 (1) Å.

† d(C1—O1) = 1.288 (1), d(C2—O2) = 1.287 (1), d(C3=O3) = 1.227 (1), d(C4=O4) = 1.230 (1), d(C1=C2) = 1.414 (1), d(C1—C4) = 1.464 (1), d(C2—C3) = 1.461 (1) Å.

SYN > *syn-SYN* according to the approximate ratios 1.00:0.94:0.94:0.70. The effect of O···O conformation is quite small in *anti-ANTI* chains [compare (*A*) and (*B*) of Fig. 3] but much greater in *syn-ANTI* (or *anti-SYN*) and *syn-SYN* chains. This last case is the most interesting. The packing scheme of DETSBR01 [(4) of Fig. 1] indicates that the *syn-SYN* chain cannot accommodate any C_2 substituent larger than hydrogen. Accordingly, substitution by bulkier groups produces a contraction of the chain to a very short *sc* or even *sp* helix [(*D*) of Fig. 3; (5) and (6) of Fig. 1]. This helix is more easily perturbed by other hydrogen bonds because the O—H···O groups are now on the outer side of the chain and can give rise to more complex windings [see (*E*) of Fig. 3 or (3′) of Fig. 2 where the α-hydroxyl groups of the ene-diolone group are the additional perturbing factor].

Hydrogen-bond strength

The d(O···O) values span the range 2.46–2.75 Å (Tables 1*b* and 2*b*), which corresponds to hydrogen bonds classified from very strong to weak (Novak, 1974; Emsley, 1980). These values bear no clear relationship to either O—H···O angles or chain type, but appear to depend only on the delocalization of the O=C—C=C—OH π-conjugated system as measured by Q or λ. Fig. 4 shows the scatterplot of d(O···O) *versus* Q and λ for all β-chains of Tables 1(*b*) and 2(*b*) plus five other β-chains not displayed in Figs. 1 and 2 but quoted in the data retrieval section, and ten more cases of intramolecular hydrogen bonds (Bertolasi *et al.*, 1991; Gilli *et al.*, 1992; Jones & Power, 1976). The general appearance of the scatterplot of d(O···O) *versus* the two π-conjugation parameters indicates that the strength of the hydrogen bond is functionally related to π-delocalization and supports the idea that the RAHB model is correct in the inter- as in the intramolecular case. On the other hand, the role played by resonance in strengthening the hydrogen bond is directly seen in the structures of (1′) and (2′) (Table 2*b*). TRIRED (1′) forms both nonresonant α- and resonant β-chains and the d(O···O) distances assume the

values of 2.744 (2) Å for the α-chain and 2.635 (2) Å for the β-chain; likewise, in REDUCA (2′) these distances are 2.746 (1) Å for the α-dimer and 2.647 (1) Å for the β-chain.

Observed O···O distances can be transformed into hydrogen-bond energies, $E_{HB} = E_{HB}(R,\delta)$ [where $R = d$(O···O) and δ = O—H···O] by the use of the Lippincott & Schroeder empirical model (Lippincott & Schroeder, 1955; Schroeder & Lippincott, 1957). Calculated E_{HB} values in kJ mol^{-1} are reported in Tables 1(*b*) and 2(*b*). They range from 13.4 to 65.3 kJ mol^{-1}, an interval of values abnormally extended on the higher energy side when compared with that of the thermodynamic E_{HB} values measured for the coupling of a variety of neutral acceptors with simple alcohols (11.3–19.7 kJ mol^{-1}) or with phenols (19.7–36.8 kJ mol^{-1}) as donors (Pimentel & McClellan, 1960, 1971). This extension of the E_{HB} scale to the 38–67 kJ mol^{-1} interval is a consequence of the resonance.

As for the rather large range of d(O···O) values observed, it has been shown (Bertolasi *et al.*, 1991) that the RAHB mechanism is highly effective only when the negative charge on the carbonyl O atom depends only on the RAHB itself and not on other charges induced by the R_3 substituent (II) or by further hydrogen bonds in which the carbonyl group is an acceptor, and that the enolic proton is systematically bonded to the O atom with the lower induced negative charge. For example, β-ketoesters give weak hydrogen bonds and their proton is never located on the side of the electron-donating —O*R* substituent. Such considerations help in understanding the d(O···O) distances of Fig. 4; β-chains made up of esters or thioesters cluster together [compounds (11), (3), (12), (4′), (5′), (9)] in a region of weaker hydrogen bonds [$2.60 \le d$(O···O) ≤ 2.68 Å] and small π-delocalization ($0.202 \le Q \le 0.244$ Å) while all β-chains derived from β-diketone enols display stronger hydrogen bonds [$2.54 \le d$(O···O) $\le$ 2.65 Å] and more delocalized π-systems ($0.127 \le Q \le 0.164$ Å).

In tetrahydroxy-*p*-benzoquinone [TOXBZQ (8′)] the abnormally long O···O distance [2.744 (5) Å] and small delocalization [$Q = 0.254$ (10) Å] are a consequence of its molecular symmetry [Fig. 2, (8′)]. The two antidromic β-chains on the opposite sides of the ring would be strengthened by positive and negative charges on the hydroxyl and carbonyl O atoms. The two carbonyl groups, however, are π-coupled in the

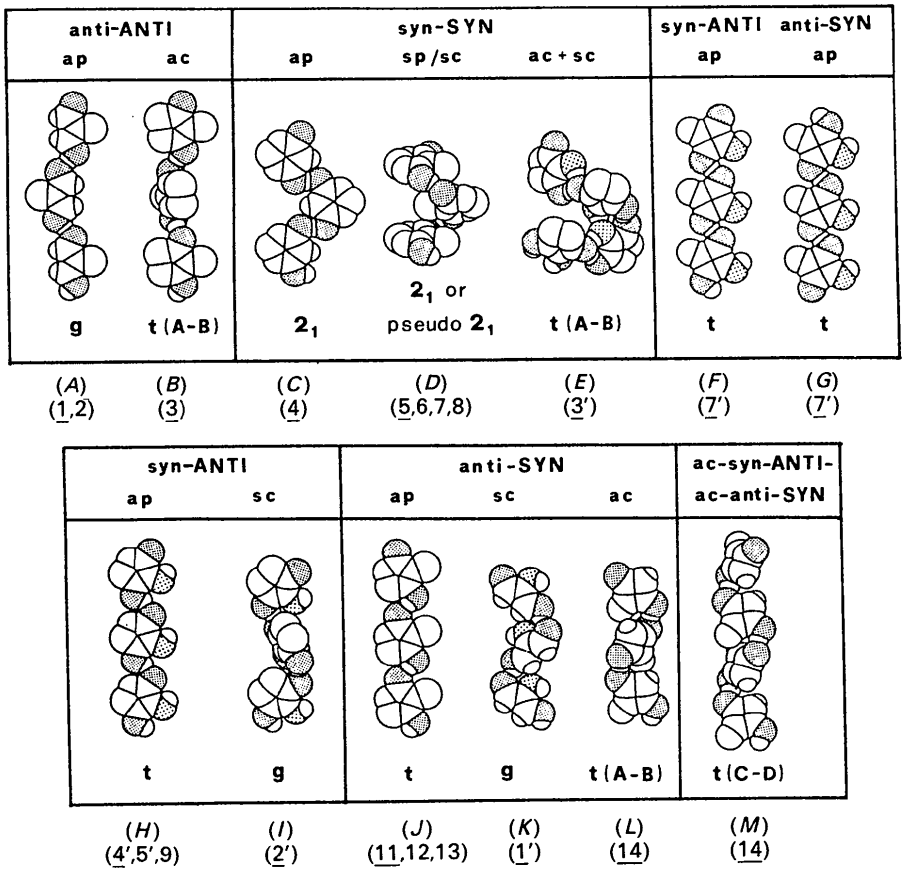


Fig. 3. Morphologies of β-chains observed in the crystal packing of enolones and enediolones of Tables 1 and 2 classified according to the crystallographic and stereochemical criteria described in the data-treatment section. 13 different types are found and indicated by the letters (*A*)–(*M*); the notation, *e.g.* (*H*): (4′, 5′, 9) means that the chain (*H*) is observed in structures (4′), (5′) and (9) of Figs. 1 and 2 and that the chain actually displayed is that underlined [*i.e.* (4′)].

anti-phase within the benzoquinone ring and this short-circuits the RAHB effect in the two opposite chains.

Deltic and squaric acids give a more complex net of intertwined β-chains and α-rings [Fig. 2, (6′) and (7′)] with rather short O—H···O bonds [d(O···O) = 2.555 (1) Å in (6′) and 2.553 (1) Å in (7′), with calculated E_{HB} values of 39.3 and 39.7 kJ mol^{-1}]. An analysis of bond distances shows, however, that hydrogen bonds are always controlled by RAHB. Pauling's bond orders (Pauling, 1947) deviate from those of the pure single and double bonds in a systematic way. Assuming standard C=O and C(sp^2)—O distances of 1.20 and 1.35 Å in enol ethers, C=C and C(sp^2)—C(sp^2) of 1.294 and 1.48 Å in cyclopropenes, and 1.335 and 1.50 Å in cyclobutenes, the bond orders calculated are those reported in italic in Fig. 5. It is seen that C—C and C—O bond orders are systematically increased and C=C and C=O bond orders decreased; moreover, bond-order changes are nearly double for the bonds where the β_1 and β_2 chains (Fig. 5) cross twice with respect to those through which the β-chains pass once, while the C_3—C_4 bond of squaric acid, not involved in the resonance, keeps its pure single-bond distance [1.500 (1) Å]. This shows that the formalism of the two intertwining β-chains correctly interprets the experimental findings.

Order–disorder transitions

The low-temperature structure of squaric acid consists of planar ferroelectric layers [Fig. 2, (7′)], antiferroelectrically stacked along **b** in the monoclinic space group $P2_1/m$ (Semmingsen, Hollander & Koetzle, 1977; Semmingsen, 1973; Wang, Stucky & Williams, 1974) and undergoes an antiferroelectric–paraelectric transition (Semmingsen & Feder, 1974; Semmingsen, 1975) near 373 K. Since (anti)ferroelectric behaviour is a potential property of all present compounds, a short discussion on squaric acid is useful to clarify the possibility of static or dynamic enolic proton disorder in their crystal structures (Herbstein, Kapon, Reisner, Lehman, Kress, Wilson, Shiau, Duesler, Paul & Curtin, 1985; Tønnesen, Karlsen & Mostad, 1982; Destro & Marsh, 1984; Vila, Lagier & Olivieri, 1990; Hall, Paul & Curtin, 1988).

At atmospheric pressure, the antiferroelectric to paraelectric phase transition occurs at the Curie temperature, T_C, of 375 K, decreases with the external pressure, is raised to 527 K by deuteration of the enolic proton and has been classified alternately as second order or mostly first order (Samara & Semmingsen, 1979; Kuhn, Petersson & Müser, 1982). Its order–disorder nature is, however, undoubtable because the high temperature $I4/m$ neutron structure (Hollander, Semmingsen & Koetzle, 1977) shows protons disordered over two equivalent positions with site occupancy 0.5 and averaged C—C, C—O and d(O···O) distances.

Data are consistent (Samara & Semmingsen, 1979; Tellgren, 1975) with a picture of the O—H···O intermolecular hydrogen bond where the proton experiences a symmetrical double-minimum potential. An increase of pressure causes a decrease of T_C by shortening d(O···O) and then lowering the inter-well energy barrier. Conversely, deuteration increases T_C by lowering the vibrational zero-point energy. Such interpretation can be extended to all present crystals because they have ordered protons under room conditions which could be disordered, in principle, by a moderate increase of temperature or pressure.

It is not easy to understand why such order–disorder transition is seldom observed and, in particular, why accurate high-pressure studies failed in

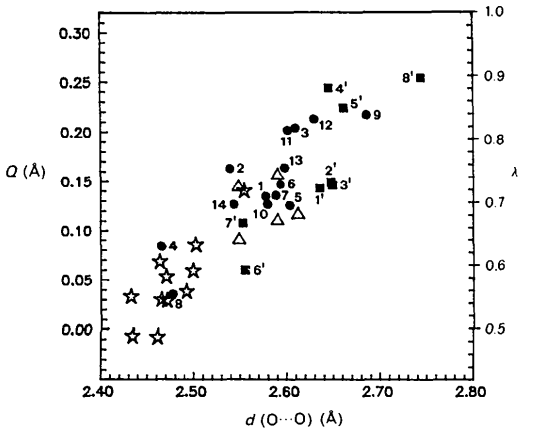


Fig. 4. Scatterplot of the π-delocalization parameters Q and λ (see text) *versus* the O···O distances for all β-chains of Tables 1 and 2 (full circles for enolones and full squares for enediolones; numbers corresponding to those used in Figs. 1 and 2). The triangles refer to the five more enolone β-chains and the stars to the ten intramolecular hydrogen bonds discussed in the text. The overall correlation coefficient is 0.89 (n = 38).

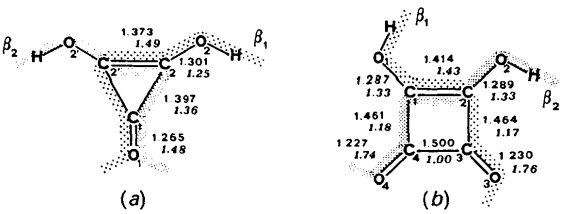


Fig. 5. Sketches of (*a*) deltic and (*b*) squaric acids reporting the relevant bond distances (Å) and, in italic, the corresponding Pauling bond orders calculated by the use of standard single- and double-bond distances given in the text. The β-chains crossing the molecules are indicated by darker or lighter shadings.

identifying it in FACRIK (2) (Katrusiak, 1990, 1991). One possible explanation comes from statistical thermodynamics. It is well known that one-dimensional lattices cannot undergo phase transitions, which become possible only for at least two-dimensional nets (Landau & Lifchitz, 1967). Most of the present crystals can be considered nearly one-dimensional because the interactions within the β-chains are much stronger than the interchain ones; therefore, they might not be able to undergo the (anti)ferroelectric–paraelectric transition because the proton movement remains confined to the one-dimensional β-chain. As a result, order–disorder transitions have been so far observed only in crystals having at least two-dimensional nets of hydrogen bonds [*e.g.* squaric acid and form *C* of naphthazarin (Herbstein *et al.*, 1985)] and their occurrence seems to be determined by the possibility of a collective motion of protons implied in more than one hydrogen bond at the same time.

Discussion and generalization

The main goal of this paper was to show that the intermolecular hydrogen bond of β-diketone enols is assisted and made stronger by the π-delocalization of the O=C—C=C—OH heterodienic system in agreement with the RAHB model already established for the intramolecular hydrogen bond (Gilli *et al.*, 1989). Present data support this hypothesis beyond any reasonable doubt because of: (i) the remarkable prevalence of resonant β-chains over other non-resonant hydrogen-bonded structures observed in crystal packings; (ii) the occurrence of abnormally short O···O contact distances in many β-chains; (iii) the strict correlation between d(O···O) values and π-delocalization indices displayed by the scatterplot of Fig. 4.

Jeffrey & Saenger (1991) have recently referred to RAHB as *π-bond cooperativity* in chained hydrogen bonding, recognizing the importance of electron polarization due to multiple covalent bonds. The two concepts are clearly equivalent on a qualitative basis, though only the RAHB model can give a quantitative appraisal of the strict relationships between d(O···O) distances, π-conjugation geometrical indices and hydrogen-bond energies.

A second point of general interest concerns the fact that crystals containing β-chains are promising candidates as organic NLO materials (Chemla & Zyss, 1987; Prasad & Williams, 1991; Desiraju, 1989) because the β-chain is a delocalizable system of conjugated π-bonds having a ground-state dipole moment and a two-state location of the proton in its double-well potential. NLO crystals, however, should contain a unique system of polar β-chains with molecular dipoles oriented at best along the main-chain direction. Our previous packing analysis may suggest some rules for obtaining such desired crystals. Firstly, all molecules where the β-diketone fragment is embedded in a ring cannot close intramolecular hydrogen bonds and are good candidates to form β-chains by RAHB strengthening, though only a proper choice of enolone substituents seems able to produce the correct alignment of molecular dipoles. The packing in Figs. 1 and 2 shows that the best orientation is given by the *ap-anti-ANTI* and *ap-syn-SYN* conformations (though *ap-syn-ANTI* or *ap-anti-SYN* might be tolerated) while in synclinal (*sc*) and synperiplanar (*sp*) O···O conformations [*e.g.* (5) and (6) of Fig. 1] molecular dipoles are unfavourably oriented with respect to the main chain. Clearly, groups liable to form further hydrogen bonds (*e.g.* most enediolones of Fig. 2) are to be avoided because of their tendency to produce convoluted chains and random dipole arrangements [*cf.* (3′) of Fig. 2].

The conditions for producing *polar* chains are much more difficult to find out since the large β-chain dipole moments (which increase with the strength of the hydrogen bond because of π-delocalization) favour centrosymmetrical chain packings. Obviously, the main way to crystal polarity is molecular chirality; in fact, out of three cases of polar β-chains observed [(3), (8), (9)], two are formed by chiral molecules [(3) and (9)]. However, chirality and a polar space group may not be sufficient, as shown by IASCOR10 (4′) and LASCAC10 (5′), in which chiral molecules form antidromic β-chains related by the 2_1 operation in space group $P2_1$. Some reduction of the molecular dipole moment may be the clue to promoting polar space groups. For instance, dipolar forces are smaller in esters or thioesters because they form weaker hydrogen bonds (Fig. 4) and, not by chance, two of the polar chains observed are in fact built up by thioester (3) or ester (9) molecules. A second method for reducing dipolar chain interactions is suggested by the packing of BEWHUG (9) (Fig. 1) where the long aliphatic substituent causes the β-chains to be stacked at the abnormally long distance of 13.8 Å.

The final point concerns the generalization of the RAHB concept to other chemical groups. In principle, it may be extended to any heteroconjugated system such as (VI*a*), where *A* and *D* are the hydrogen-bonding donor and acceptor (mainly O and N but also S atoms), *N* is a positive integer including zero and $n = 2N + 1$ is the odd number of atoms in the conjugated chain connecting *A* and *D*. Such a fragment is a resonance hybrid between (VI*a*) and (VI*b*) and it is suited to form hydrogen bonds which are resonance assisted. Assigning to (VI*a*) the graphical symbol (VII*a*), its possible self-aggregation modes are seen to be dimers (VIII) [or larger rings as

in (10) of Fig. 1], infinite chains (X) or closed rings (IX). A variety of chemical groups can be represented by changing *A*, *D* and *n*. Taking into account only O and N atoms, the first-order term (VII*b*) can depict carboxylic acids O=C*R*—OH and amides O=C*R*—NH*R*, compounds well known to form dimers (VIII) or chains (X) connected by hydrogen bonds, as well as amidines N*R*=C—NH*R*. This last fragment is present in imidazoles for which an example of hydrogen-bonded chain (X) is shown in Fig. 6 (Bouwman & Driessen, 1989); the average N···N contact distance of 2.813 (5) Å is on the short side of its accepted range of 2.75–3.15 Å (Saenger, 1983) and the contribution of the polar form to the resonance $RN{=}C{-}NHR \leftrightarrow RN^{-}{-}C{=}N^{+}HR$ amounts (Pauling, 1947) to 41%. The second-order term (VII*c*) may be represented by enolones (or β-diketone enols) and enaminones, O=C—C=C—NH*R*. The former are described here in their aggregation form (X) and have been already treated (Bertolasi *et al.*, 1991) in the intramolecular situation (IX). Two examples of enaminone hydrogen-bonding are shown in Figs. 7 and 8. In the intermolecular case (X) the N···O distance is 2.694 (3) Å (Ferretti, Bertolasi, Gilli & Borea, 1985) (one of the shortest intermolecular distances so far observed) and the contribution of the polar form to the conjugated system amounts to 39%, while the intramolecular linking (IX) is characterized by a slightly shorter N···O length [2.653 (8) Å (Diánez, López-Castro & Márquez, 1988)] and an almost complete π-delocalization. Higher terms of the O—H···O series ($n = 5$: δ-diketone enols; $n = 7$: ξ-diketone enols) have also been reported (Gilli & Bertolasi, 1990) to form very strong intramolecular hydrogen bonds (IX) [O···O distances as low as 2.425 (6) Å (Drück & Littke, 1980)].

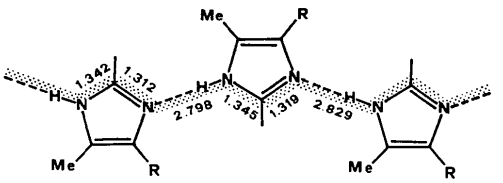


Fig. 6. The crystal packing of JATDIR. The shading marks the resonant chain of intermolecular hydrogen bonds made by the enamine fragments. Distances are given in Å.

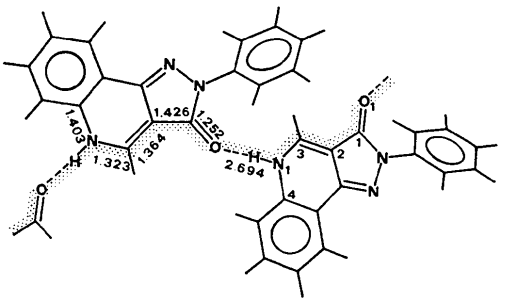


Fig. 7. The crystal packing of COVLII. The shading indicates the resonant β-chain formed by the enaminone fragments. Distances are given in Å.

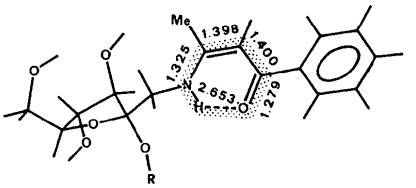
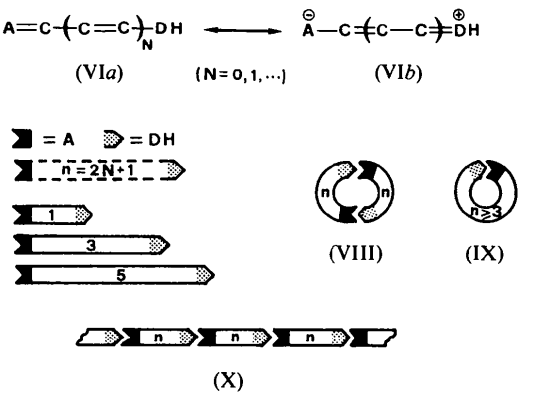


Fig. 8. The molecular structure of GEMYEC. The resonant intramolecular hydrogen bond formed by the enaminone fragment is marked by shading. Distances are given in Å.



Hydrogen bonds formed by some of the shortest terms (amides and amidines) are of biological relevance. It has already been remarked that purine–pyrimidine base pairing in DNA [basically obtained by the amide–amidine couplings (VIII)] is assisted by resonance or, in slightly different words, hydrogen bond π-cooperativity; similar considerations were suggested for the resonant amide chains (X) which are found both in α-helices and β-pleated sheets of proteins (Gilli *et al.*, 1989; Jeffrey & Saenger, 1991; Saenger, 1983). This suggests that nature itself may have taken advantage of the greater energy of RAHB to keep control of molecular associations whose stability is essential to life.

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References

ALDEN, R. A., STOUT, G. H., KRAUT, J. & HIGH, D. F. (1964). *Acta Cryst.* **17**, 109–121.

ALLEN, F. H., BELLARD, S., BRICE, M. D., CARTWRIGHT, B. A., DOUBLEDAY, A., HIGGS, H., HUMMELINK, T., HUMMELINK-PETERS, B. G., KENNARD, O., MOTHERWELL, W. D. S., RODGERS, J. R. & WATSON, D. G. (1979). *Acta Cryst.* B**35**, 2331–2339.

ALLEN, F. H., KENNARD, O., WATSON, D. G., BRAMMER, L., ORPEN, A. G. & TAYLOR, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.

AZARNIA, N., BERMAN, H. M. & ROSENSTEIN, R. D. (1971). *Acta Cryst.* B**27**, 2157–2161.

BERTOLASI, V., GILLI, P., FERRETTI, V. & GILLI, G. (1991). *J. Am. Chem. Soc.* **113**, 4917–4925.

BIDEAU, J. P., BRAVIC, G. & FILHOL, A. (1977). *Acta Cryst.* B**33**, 3847–3849.

BOUWMAN, E. & DRIESSEN, W. L. (1989). *Acta Cryst.* C**45**, 1792–1794.

CECCARELLI, C., JEFFREY, G. A. & TAYLOR, R. (1981). *J. Mol. Struct.* **70**, 255–271.

CHAMBERS, M. S., THOMAS, E. J. & WILLIAMS, D. J. (1987). *J. Chem. Soc. Chem. Commun.* pp. 1228–1230.

CHEMLA, D. S. & ZYSS, J. (1987). *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vols. 1, 2. Orlando: Academic Press.

DESIRAJU, G. R. (1989). *Crystal Engineering. The Design of Organic Solids*. Amsterdam: Elsevier.

DESTRO, R. & MARSH, R. E. (1984). *J. Am. Chem. Soc.* **106**, 7269–7271.

DIÁNEZ, M. J., LÓPEZ-CASTRO, A. & MÁRQUEZ, R. (1988). *Acta Cryst.* C**44**, 657–660.

DRÜCK, U. & LITTKE, W. (1980). *Acta Cryst.* B**36**, 3002–3007.

EMSLEY, J. (1980). *J. Chem. Soc. Rev.* **9**, 91–124.

EMSLEY, J. (1984). *Struct. Bonding*, **57**, 147–191.

EMSLEY, J., MA, L. Y. Y., BATES, P. A., MOTEVALLI, M. & HURSTHOUSE, M. B. (1989). *J. Chem. Soc. Perkin Trans.* 2, pp. 527–533.

ETTER, M. C. (1990). *Acc. Chem. Res.*, **23**, 120–126.

ETTER, M. C., HOYE, R. C. & VOJTA, G. M. (1988). *Crystallogr. Rev.* **1**, 281–338.

ETTER, M. C., MACDONALD, J. C. & BERNSTEIN, J. (1990). *Acta Cryst.* B**46**, 256–262.

ETTER, M. C., URBANCZYK-LIPKOWSKA, Z., JAHN, D. A. & FRYE, J. S. (1986). *J. Am. Chem. Soc.* **108**, 5871–5876.

ETTER, M. C. & VOJTA, G. M. (1989). *J. Mol. Graphics*, **7**, 3–11.

FENG, X., BOTT, S. G. & LIPPARD, S. J. (1990). *Acta Cryst.* C**46**, 1671–1674.

FERRETTI, V., BERTOLASI, V., GILLI, G. & BOREA, P. A. (1985). *Acta Cryst.* C**41**, 107–110.

FLORIS, B. (1990). *The Chemistry of Enols*, edited by Z. RAPPOPORT, ch. 4. New York: John Wiley.

FRISCH, M. J., SCHEINER, A. C., SCHAEFER, H. F. III & BINKLEY, J. S. (1985). *J. Chem. Phys.* **82**, 4194–4198.

GAVUZZO, E., MAZZA, F., CAROTTI, A. & CASINI, G. (1984). *Acta Cryst.* C**40**, 1231–1233.

GILLI, G., BELLUCCI, F., FERRETTI, V. & BERTOLASI, V. (1989). *J. Am. Chem. Soc.* **111**, 1023–1028.

GILLI, G. & BERTOLASI, V. (1990). *The Chemistry of Enols*, edited by Z. RAPPOPORT, ch. 13. New York: John Wiley.

GILLI, P., FERRETTI, V., BERTOLASI, V. & GILLI, G. (1992). *Acta Cryst.* C**48**, 1798–1801.

GÖRBITZ, C. H., MOSTAD, A., PEDERSEN U., RASMUSSEN, P. B. & LAWESSON, S.-O. (1986). *Acta Chem. Scand. Ser. B*, **40**, 420–429.

GRAVES, B. J. & HODGSON, D. J. (1981). *Acta Cryst.* B**37**, 1576–1584.

HALL, R. C., PAUL, I. C. & CURTIN, D. Y. (1988). *J. Am. Chem. Soc.* **110**, 2848–2854.

HERBSTEIN, F. H., KAPON, M., REISNER, G. M., LEHMAN, M. S., KRESS, R. B., WILSON, R. B., SHIAU, W.-I., DUESLER, E. N., PAUL, I. C. & CURTIN, D. Y. (1985). *Proc. R. Soc. London. Ser A*, **399**, 295–319.

HOLLANDER, F. J., SEMMINGSEN, D. & KOETZLE, T. F. (1977). *J. Chem. Phys.* **67**, 4825–4831.

HVOSLEF, J. (1968). *Acta Cryst.* B**24**, 1431–1440.

JEFFREY, G. A. & SAENGER, W. (1991). *Hydrogen Bonding in Biological Structures*, ch. 2, p. 37. Berlin: Springer.

JONES, R. D. G. & POWER, L. F. (1976). *Acta Cryst.* B**32**, 1801–1806.

KATRUSIAK, A. (1989). *Acta Cryst.* C**45**, 1897–1899.

KATRUSIAK, A. (1990). *Acta Cryst.* B**46**, 246–256.

KATRUSIAK, A. (1991). *Acta Cryst.* B**47**, 398–404.

KLUG, H. P. (1965). *Acta Cryst.* **19**, 983–992.

KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–525.

KOPTEVA, T. S. & SHIGORIN, D. N. (1974). *Russ. J. Phys. Chem.* **48**, 312–314.

KROGH ANDERSEN, E. & KROGH ANDERSEN, I. G. (1975). *Acta Cryst.* B**31**, 394–398.

KROGH ANDERSEN, E., KROGH ANDERSEN, I. G. & PLOUG-SØRENSEN, G. (1987). *Acta Chem. Scand. Ser. A*, **41**, 213–217.

KROON, J., KANTERS, J. A., VAN DUIJNEVELDT-VAN DE RIJDT, J. G. C. M., VAN DUIJNEVELDT, F. B. & VLIEGENTHART, J. A. (1975). *J. Mol. Struct.* **24**, 109–129.

KUHN, W., PETERSSON, J. & MÜSER, H. E. (1982). *Phys. Status Solidi A*, **71**, 483–490.

KULESHOWA, L. N. & ZORKY, P. M. (1980). *Acta Cryst.* B**36**, 2113–2115.

LANDAU, L. & LIFCHITZ, E. (1967). *Physique Statistique*, p. 567. MOSCOW: MIR.

LIPPINCOTT, E. R. & SCHROEDER, R. (1955). *J. Chem. Phys.* **23**, 1099–1106.

LOW, J. N. & WILSON, C. C. (1983). *Acta Cryst.* C**39**, 1688–1690.

MEESTER, P. DE, JOVANOVICH, M. V., CHU, S. S. C. & BIEHL, E. R. (1986). *J. Heterocycl. Chem.* **23**, 337–342.

NORRESTAM, R., VON GLEHN, M. & WACHTMEISTER, C. A. (1974). *Acta Chem. Scand. Ser. B*, **28**, 1149–1152.

NOVAK, A. (1974). *Struct. Bonding*, **18**, 177–216.

PAULING, L. (1947). *J. Am. Chem. Soc.* **69**, 542–553.

PIMENTEL, G. C. & MCCLELLAN, A. L. (1960). *The Hydrogen Bond*. San Francisco: Freeman.

PIMENTEL, G. C. & MCCLELLAN, A. L. (1971). *Annu. Rev. Phys. Chem.* **22**, 347–385.

PRASAD, P. N. & WILLIAMS, D. J. (1991). *Introduction to Nonlinear Optical Effects in Molecules and Polymers*. New York: John Wiley.

SAENGER, W. (1983). *Principles of Nucleic Acids Structure*, ch. 6, p. 118. New York: Springer.

SAMARA, G. A. & SEMMINGSEN, D. (1979). *J. Chem. Phys*, **71**, 1401–1407.

SCHÖNWÄLDER, K. H., KOLLAT, P., STEZOWSKI, J. J. & EFFENBERGER, F. (1984). *Chem. Ber.* **117**, 3280–3296.

SCHROEDER, R. & LIPPINCOTT, E. R. (1957). *J. Phys. Chem.* **61**, 921–928.

SCHWALBE, C. H. & SAENGER, W. (1973). *Acta Cryst.* B**29**, 61–69.

SEMMINGSEN, D. (1973). *Acta Chem. Scand.* **27**, 3961–3972.

SEMMINGSEN, D. (1974*a*). *Acta Chem. Scand. Ser. B*, **28**, 169–174.

SEMMINGSEN, D. (1974*b*). *Acta Chem. Scand. Ser. B*, **28**, 141–147.

SEMMINGSEN, D. (1975). *Acta Chem. Scand. Ser. A*, **29**, 470–473.

SEMMINGSEN, D. (1977*a*). *Acta Chem. Scand. Ser. B*, **31**, 81–85.

SEMMINGSEN, D. (1977*b*). *Acta Chem. Scand. Ser. B*, **31**, 114–118.

SEMMINGSEN, D. & FEDER, J. (1974). *Solid State Commun.* **15**, 1369–1372.

SEMMINGSEN, D. & GROTH, P. (1987). *J. Am. Chem. Soc.* **109**, 7238–7239.

SEMMINGSEN, D. & GROTH, P. (1988). *Acta Chem. Scand. Ser. B*, **42**, 1–6.

SEMMINGSEN, D., HOLLANDER, F. J. & KOETZLE, T. F. (1977). *J. Chem. Phys.* **66**, 4405–4412.

TELLGREN, R. (1975). Doctoral Thesis. *Acta Univ. Ups.* **344**.
TØNNESEN, H. H., KARLSEN, J. & MOSTAD, A. (1982). *Acta Chem. Scand. Ser. B*, **36**, 475–479.
TRIFONOV, L., BIERI, J. H., PREWO, R., DREIDING, A. S., RAST, D. M. & HOESCH, L. (1982). *Tetrahedron*, **38**, 397–403.
VILA, A. J., LAGIER, C. M. & OLIVIERI, A. C. (1990). *J. Chem. Soc. Perkin Trans.* 2, pp. 1615–1618.
WANG, Y., STUCKY, G. D. & WILLIAMS, J. M. (1974). *J. Chem. Soc. Perkin Trans.* 2, pp. 35–38.
ZVILICHOVSKY, G. (1987). *J. Heterocycl. Chem.* **24**, 465–470.

Book Reviews

Works intended for notice in this column should be sent direct to the Book-Review Editor (R. F. Bryan, Department of Chemistry, University of Virginia, McCormick Road, Charlottesville, Virginia 22901, USA). As far as practicable, books will be reviewed in a country different from that of publication.

Acta Cryst. (1993). B**49**, 576

Organic crystal chemistry. (IUCr Crystallographic Symposia No. 4.) Edited by J. B. GARBARCZYK and D. W. JONES. Pp. xi + 203. Oxford University Press, 1991. Price £30.00, US $55.00. ISBN 0-19-855383-8.

This book contains a cross-section of the papers presented at the Seventh Symposium on Organic Crystal Chemistry, organized by Professor Z. Kałuski of the Faculty of Chemistry at Adam Mickiewicz University, and held at Poznań-Rydzyna, Poland, 14-17 August 1989. These symposia have provided a forum for interaction between the sizable Polish chemical crystallographic community and a significant number of chemical crystallographers from other countries. The field of organic crystal chemistry has moved beyond the basic experimental determination of molecular dimensions to consideration of the chemical, biological and physical properties of both molecules and the crystals in which they find themselves. The papers in this volume deal with a wide range of current topics in crystal chemistry, including the arrangement of molecules in crystals (studies of polymorphism and crystal engineering), analysis and prediction of intermolecular interactions, studies of the properties of solid solutions, and identification of structural trends - found by surveying the wealth of data available from crystallographic databases.

This book is an excellent introduction to these various applications of crystallographic studies and should be placed in the hands of any young person considering a career in crystal chemistry. It is an admirable refutation of the misperception of many scientists that crystallography is a service rather than a scientific study.

A strong theme in the volume is the study, analysis and control of intermolecular interactions. The book begins with J. Bernstein's elegant presentation of polymorphism and its implications for the properties of crystalline materials, and of molecules, that depend strongly on conformation. D. Paukstza and coworkers present a cleverly designed device for growing crystals in an electric field and thereby affecting polymorphism. A chapter on controlling crystal growth through solvent-surface interactions (by L. Shimon, M. Vaida, L. Addadi, M. Lahav and L. Leiserowitz) continues the emphasis on intermolecular interactions and their role in determining crystal properties. T. Krygowski's paper provides mathematical tools helpful in the analysis of interactions, and examples of such interactions are presented by A. Katrusiak in a study of β-diketoalkanes.

The chemistry or biology of molecules is another theme in the book and is represented in articles on the steroid hormone receptor (W. Duax and J. Griffin), Werner clathrates (Z. Lipkowska), cycloannulated aromatic systems (R. Boese and coworkers), S→O hypervalent bonds (A. Kálmán) and aryl oxide-aluminium π-bonding (A. Barron). These papers demonstrate the power of a study that joins detailed analysis of individual structure determinations to the analysis of a large number of similar structures to identify chemical properties or predict biological actions.

The volume is carefully prepared and edited in all but one respect. The exception relates to the linkage between text and illustrations. As is often the case with papers prepared from oral presentations, although the papers are clear and well illustrated, the illustrations are often not explained adequately in the text, or are captioned unclearly. However, overall this volume is important reading for anyone working in the field of crystal chemistry.

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Crystallography in modern chemistry. A resource book of crystal structures. By THOMAS C. W. MAK and GONG-DU ZHOU. Pp. xiii + 1323. New York: John Wiley, 1992. Price $136.00. ISBN 0-471-54702-6.

This book is based on lectures of the authors at the Chinese University of Hong Kong, the University of Western Ontario and Peking University over the past 25 years. It is a tribute to the richness of structural data obtained by X-ray crystallographic studies. The first 20 pages consist of a historical review of crystal structure determinations. Then follow details of structure determinations and discussions of their significance