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The Hydrogen-Bond C—H Donor and π-Acceptor Characteristics of Three-Membered Rings

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Abstract

Crystallographic results, retrieved from the Cambridge Structural Database, show that the C—H protons of cyclopropane, aziridine and oxirane form C—H$\cdots$O (particularly C—H$\cdots$O=C) hydrogen bonds. The frequency of formation and geometrical characteristics of these bonds indicate a bond-strength ordering: Csp^1—H$\cdots$O > C(ring)—H$\cdots$O $\simeq$ Csp^2—H$\cdots$O > Csp^3—H$\cdots$O, which is in excellent agreement with the well known ethylenic properties of C(ring)—H and with residual $\delta+$ charges calculated for these systems. There is some evidence to suggest that C=C—H in cyclopropene, known to be a highly acidic H, forms stronger hydrogen bonds than C—H in saturated three-membered rings. Crystallographic data have also been used to provide geometrical evidence for the formation of O,N—H$\cdots\pi$(ring) bonding to three-membered rings, proposed on the basis of spectroscopic data [Joris, Schleyer & Gleiter (1968). *J. Am. Chem. Soc.* **90**, 327–336]. The two modes of H$\cdots\pi$(ring) binding suggested there, *viz*. 'edge-on' approach of H to a ring C—C bond and 'face-on' approach towards the ring centroid, are found to be dominant in crystallographic observations of this novel hydrogen bond.

1. Introduction

Despite early controversies (Sutor, 1963; Donohue, 1968) that first enhanced and then contradicted a growing body of spectroscopic data, crystallographic evidence for the existence of C—H$\cdots X$ hydrogen bonds is now both well established (Taylor & Kennard, 1982) and increasingly well documented (Desiraju, 1991, Jeffrey & Saenger, 1991). Although weak (~4–10 kJ mol^{-1}), these bonds, and particularly the C—H$\cdots$O bond, are now seen as important secondary interactions in biological structures and can become primary, *i.e.* structure determining, in some small-molecule structures.

A continuing area of interest has been to establish the relative donor abilities of C—H from different chemical environments. An early review of spectroscopic data (Allerhand & Schleyer, 1963) indicated that donor abilities decreased in the order Csp^1—H > Csp^2—H > Csp^3—H. The review also indicated that, in the latter case, a strong electron-withdrawing group attached to Csp^3 was probably an essential factor in proton donation to O acceptors. This general H-acidity requirement was noted by Taylor & Kennard (1982) and has recently been confirmed and systematically studied by Pedireddi & Desiraju (1992). Here, the C$\cdots$O distances in C—H$\cdots$O hydrogen bonds, incorporating a wide variety of C hybridizations and substitution patterns, are shown to correlate well with pK_a (Me_2SO) values, thus providing a novel scale of carbon acidity based upon C$\cdots$O distances in these systems.

One group of compounds with special C-hybridization characteristics, and one that has received little attention as possible proton donors, is the class of three-membered ring compounds. It is well known that cyclopropane exhibits chemical properties that are analogous to alkenes rather than alkanes (Charton, 1970). It has been shown theoretically (see, *e.g.* Hoffman, 1970; Hoffman & Stohrer, 1971) and from crystallographic data (Allen, 1980, 1981) that cyclopropane (I) uses $\sim sp^{4.2}$ hybrids in ring-bond formation and, most importantly, uses $\sim sp^{2.2}$ hybrids (31% *s*-character) in forming bonds to the exocyclic H atoms. Due to electronegativity differences between C and N in aziridine (II) and C and O in oxirane (III), the exocyclic percentage *s*-character increases slightly, reaching almost exactly 33% in (III) (Allen, 1982*a*). In cyclopropene (IV) the methylene group is cyclopropane-like, while the double bond has acetylenic properties (Closs, 1966). Geometrical data indicate that the unsaturated C(2,2′) atoms in (IV) use $\sim sp^{1.2}$ hybrids in forming bonds to exocyclic H atoms (Allen, 1982*b*). Given these anomalies, it is of interest to examine the geometry of short C(ring)—H$\cdots X$ contacts in crystal structures containing (I)–(IV) and appropriate acceptor atoms, and to see if mean C$\cdots$O distances extend the acidity correlation of Pedireddi & Desiraju (1992). For completeness here, we compare our results for C—H$\cdots X$ systems involving (I)–(IV) with analogous

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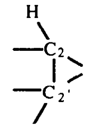
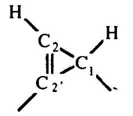
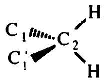
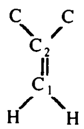
data for C—H in fully saturated (V), terminal methylene (VI) and acetylenic (VII) environments.



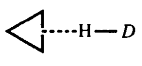


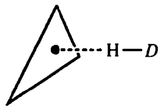
(I) $X = C<$ (cyclopropane) (IV) cyclopropene
(II) $X = N$ (aziridine)
(III) $X = O$ (oxirane)





(V) (VI) (VII) (Y = any atom)





(VIIIa) (VIIIb)

Spectroscopic evidence for the existence of O,N—H···π hydrogen bonding to acetylenic, olefinic and aromatic acceptors is well documented (Joris, Schleyer & Gleiter, 1968, and references therein). Recently, Viswamitra, Radhakrishnan, Bandekar & Desiraju (1993) have presented a survey of available crystallographic data and have shown that intermolecular examples of these bonds are clearly observed in crystal structures. Although they are not common, these weak hydrogen bonds are shown to be both structurally and energetically significant. More recently, Steiner (1995*a*,*b*) has presented novel crystal structures, database evidence and quantum chemical calculations on C≡C—H···π(C≡C) and π(phenyl) bonding. He tabulates 11 H···C≡C(midpoint) distances in the range 2.51–2.87 Å and eight H···phenyl centroid distances from 2.51 up to his imposed limit of 2.80 Å. Hydrogen-bond cooperativity is observed in extended H···π(C≡C) systems and his calculations indicate bond energies in the range 4.2–9.2 kJ mol^{-1}.

Joris, Schleyer & Gleiter (1968) also used IR spectroscopy to investigate the ability of cyclopropane rings to accept O—H protons in both intra- and intermolecular interactions. This conjecture was made on the basis, again, of the ethylenic properties of cyclopropane (cp) and the spectroscopic evidence is strongly in favour of O—H···cp interactions. Two geometries were proposed, the edge-on model (VIII*a*) and the face-on model (VIII*b*), of which the former was considered to be preferred, at least in their intramolecular cases, due to stereochemical constraints in the molecules studied. Model (VIII*a*) would also seem most likely in other cases due to the bent or 'banana' form of the intra-annular bonds in three-membered rings, leading to local electron density maxima in the ring plane but outside the three direct interatomic vectors. This density is clearly visible in the accurate charge-density analyses of Nijveldt & Vos (1988*a*,*b*,*c*). In this paper we extend the studies of Viswamitra *et al.* (1993) and Steiner (1995*a*,*b*) to try to locate crystallographic evidence for the N,O—H···cp interactions so clearly identified by Joris, Schleyer & Gleiter (1968).

2. Methodology

2.1. *Database searches*

The October 1994 and April 1995 releases of the Cambridge Structural Database System (CSDS: Allen *et al.*, 1991), denoted as releases 5.08 and 5.09 containing 126 353 and 140 236 entries, respectively, were used in this work. Searches for bonded substructures and intra- and intermolecular non-bonded contacts were carried out using the program *QUEST3D* (Cambridge Structural Database System User's Manual, 1994). Subsequent data analyses were performed using *VISTA* (Cambridge Structural Database System User's Manual, 1995).

The general search fragment for C—H···acceptor interactions is shown in Fig. 1(*a*). Substructures were only located in entries that: (*a*) were organic compounds

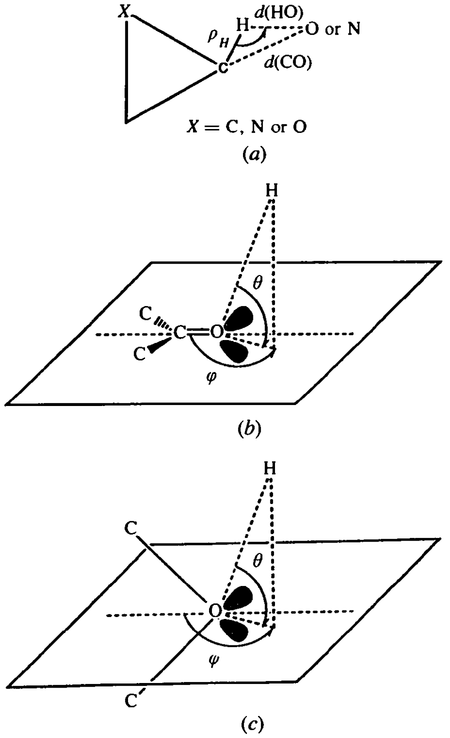


Fig. 1. (*a*) General search fragment for C(ring)—H···acceptor contacts, (*b*) lone-pair directionality parameters (θ, φ) for (*b*) >C=O sp^2 and (*c*) —O— sp^3 lone pairs.

Table 1. *Geometrical constraints used in non-bonded contact searches for C—H···O or N systems using the CSD program QUEST3D (parameters are defined in Fig. 1)*

Parameter	Criteria *A**	Criteria *B*
d(HO) or *d*(HN) (max) (Å)	3.0	2.9
d(CO) or *d*(CN) (max) (Å)	4.0	3.9
ρ_H (°)	110–180	120–180
$\lvert\varphi\rvert$ (°)	Any	60–180

* Desiraju (1991) and Pedireddi & Desiraju (1992).

Table 2. *Numbers of C—H···O or N contacts (geometrical criteria A of Table 1) formed by rings I, II and III to various acceptors*

	Donor C—H from		
Acceptor	I	II	III
C=O	410	79	235
H_2O	9	0	5
C—OH	34	10	66
C—O—C	29	8	292
C—NH_2	2	0	0
C—NH—C	0	7	1
C—NC—C	4	4	2
C=N—C	11	9	1

Table 3. *Residual charges (electrons) on C, H, N and O atoms of (I)–(VI) and the open-chain analogues of (I)–(III) (propane, dimethylamine, dimethylether, see text) as calculated by GAMESS-UK (Guest et al., 1993) using full geometry optimization and the 6-31G** basis set*

In (I) C1 and C2 are symmetry equivalent; in (II) the H atoms at C2 are described as *syn* or *anti* to the H atom on N1.

Molecule	Atom	Residual charges	Residual charges (Open-chain analogues)
(I) Cyclopropane	C1	−0.261	−0.220
	H(C1)	+0.131	+0.110
	C2		−0.340
	H(C2)		+0.110
(II) Aziridine	N1	−0.568	−0.621
	H(N1)	+0.276	+0.265
	C2	−0.116	−0.139
	$H(C2)_{syn}$	+0.123	+0.080 to +0.120
	$H(C2)_{anti}$	+0.139	
(III) Oxirane	O1	−0.553	−0.609
	C2	+0.015	−0.006
	H(C2)	+0.131	+0.090 to +0.120
(IV) Cyclopropene	C1	−0.242	
	H(C1)	+0.104	
	C2	−0.141	
	H(C2)	+0.158	
(V) Propane (central CH_2)	C2	−0.340	
	H(C2)	+0.110	
(VI) Ethylene	C1	−0.254	
	H(C1)	+0.127	
(VII) Acetylene	C1	−0.233	
	H(C1)	+0.233	

within CSD chemical class definitions, (*b*) had error-free coordinate sets in CSD check procedures, (*c*) exhibited no crystallographic disorder, (*d*) contained no polymeric (catena) connections and (*e*) had a crystallographic $R \leq 0.075$. All H atoms involved in non-bonded contact searches were placed in normalized positions, *i.e.* they were repositioned along their X-ray determined C—H, N—H or O—H vectors at a distance from C,N,O equal to the appropriate mean bond length established from neutron studies (Allen *et al.*, 1987).

Non-bonded contact searches and geometrical analyses of interactions involving ring C—H atoms as proton donors to oxygen acceptors were carried out in terms of the parameters indicated on Fig. 1(*a*), *viz.* *d*(HO) and *d*(CO) in Å, and the hydrogen-bond angle ρ_H = C—H···O. Additionally, for sp^2 and sp^3 hybridized acceptor atoms, *i.e.* >C=O (Fig. 1*b*) and C—O—C (Fig. 1*c*), we calculated absolute values of the spherical polar angles θ and φ that describe the elevation (θ) and rotation (φ) of the H···*A* vector with respect to the putative lone-pair planes. Special searches and geometrical parameters that relate to the study of three-membered rings as π-acceptors in N,O—H···π interactions are described in a later section.

For C—H···acceptor searches (Fig. 1*a*), we began by using the limiting geometrical criteria (Table 1) that had already been defined and justified elsewhere (Desiraju, 1991; Pedireddi & Desiraju, 1992). We refer to these constraints as criteria *A* in associated text and tables. Later we introduced an additional criterion involving the H-approach angle φ (Figs. 1*b* and *c*) and modified the initial constraints slightly to generate criteria *B* (Table 1). Table 2 shows the number of C—H···acceptor contacts, within criteria *A*, that are formed by C—H atoms of rings I, II and III to a variety of O- and N-acceptors. Clearly, the numbers of C—H···N contacts are very small and further attention concentrated on the characterization of the more highly populated C—H···O acceptor groups.

2.2. *Molecular orbital calculations*

Ab initio molecular orbital calculations were carried out to provide a comparative overview of residual atomic charges for the C,N—H atoms among molecules (I)–(VI) and for the open-chain analogues of rings (I)–(III), *i.e.* propane, dimethylamine and dimethyl ether, which are obtained by breaking the C2—C2′ bond. The *GAMESS-UK* package (Guest *et al.*, 1993) was used and closed-shell self-consistent field (restricted Hartree–Fock) calculations were carried out using the 6-31G** basis set with full geometry optimization. Partial charges, q_j, were obtained by Mullikan population analysis and the results are given in Table 3.

The partial charges on H atoms (q_H) attached to rings I–III are almost identical at +0.131 e, although q_H for C—H_{syn} and C—H_{anti} in aziridine vary marginally (and equally) either side of this value. As expected, the q_H for ring protons is closely comparable to that for the

Table 4. *Extended results of substructure searches for C—H···O contacts formed by I, II, III, V, VI, VII and oxygen acceptors*

Four lines of information are given for each donor–acceptor combination: line 1 has n_1: n_2, where n_1 is the number of available C—H donors and n_2 is the number of available acceptor O atoms; line 2 gives the ratio n_1: n_2; line 3 gives $n_3(n_3/n_1\,\%)$, where n_3 is the number of C—H···O contacts located using criteria *A* of Table 1;. line 4 gives $n_4(n_4{:}n_1\,\%)$, where n_4 is the number of C—H···O contacts located using criteria *B* of Table 1.

Acceptor	Donor C—H from					
	(I)	(II)	(III)	(V)	(VI)	(VII)
C=O	1253:785	235:178	679:745	5910:2092	1586:1324	61:75
	1.596	1.320	0.911	2.825	1.198	0.813
	410 (32.7)	79 (33.6)	235 (34.6)	1034 (17.5)	336 (21.2)	29 (47.5)
	327 (26.1)	63 (26.8)	181 (26.7)	740 (12.5)	250 (15.8)	21 (34.4)
C=O*†	711:472	71:57	391:428	2750:859	720:582	22:27
	1.506	1.246	0.914	3.201	1.237	0.815
	248 (34.9)	41 (57.7)	153 (39.1)	534 (19.4)	167 (23.2)	16 (72.7)
	195 (27.4)	35 (49.3)	116 (29.7)	384 (14.0)	132 (18.3)	15 (68.2)
C—O—H	340:144	39:19	384:315	7052:1319	842:597	63:75
	2.361	2.05	1.219	5.347	1.410	0.840
	34 (10.0)	10 (25.6)	66 (17.2)	522 (7.4)	81 (9.6)	26 (41.3)
	15 (4.4)	8 (20.5)	58 (15.1)	360 (5.1)	56 (6.7)	24 (38.1)
C—O—C	258:132	41:25	1044:926	6944:2000	544:415	25:34
	1.954	1.640	1.127	3.472	1.311	0.735
	29 (11.2)	8 (19.5)	292 (27.9)	344 (4.9)	54 (9.9)	12 (48.0)
	24 (9.3)	6 (14.6)	214 (20.5)	344 (4.9)	44 (8.1)	11 (44.0)

† Data from CSD entries that contain no O—H or N—H donors.

methylene protons in (VI). Both these values, 0.131 (I–III) and 0.127e (VI), are larger than the q_H for methyl protons (0.080–0.120e) calculated for the C2—H of the open-chain analogues of (I)–(III). They are, however, very much lower than the $q_H = +0.233$e calculated for acetylenic H atoms (VII). *Ab initio* results for cyclopropene (IV) are interesting. The residual charge on the C2sp^2—H proton is larger than for Csp^3—H in (I)–(III) and Csp^2—H in (VI), but is smaller than Csp^1—H acetylene (VII), as is predictable from the hybridization models for (IV) (Allen, 1982*b*), as summarized above. However, C1sp^3—H protons in (IV) have $q_H = +0.104$e, a value more typical of Csp^3—H in non-ring environments (V) and indicative of an exocyclic C1-substituent hybrid that is closer to sp^3 than the $sp^{2.2}$ of C1 in (I)–(III).

3. The C—H donor properties of three-membered rings

3.1. *Summary statistics for C—H···O fragments*

Table 4 gives extensive substructure search statistics for the O acceptors C=O, C—O—H and C—O—C. Here we report the numbers of C—H donors (n_1) and O acceptors (n_2) that exist in those CSD entries which contain at least one donor and one acceptor group, whether they are in contact or not. Also reported are n_3 and n_4, the numbers of C—H···O contacts actually located in each donor–acceptor class using criteria *A* (n_3) or *B* (n_4) of Table 1.

Table 4 also incorporates comparative results for searches involving C—H donors from substructures (V), (VI) and (VII). In the case of the terminal methylene and acetylenic protons of (VI) and (VII), all CSD entries that passed the acceptance criteria applied to (I), (II) and (III) were examined for C—H···O contacts. For substructure (V), data were assembled from database subsets comprising the first 1000 CSD entries that contained (*a*) a >C=O acceptor, (*b*) a C—O—H acceptor or (*c*) a C—O—C acceptor. Further, only C—H···O contacts involving C_2—H in (V) were considered (to preserve a chemical analogy with the ring C—H protons and to avoid the use of terminal—CH_3 protons).

Obviously, the numbers of C—H···O contacts formed (n_3, n_4) depend upon the relative availabilities of donor(s) and acceptor(s) within the individual structures that comprise each dataset. However, the data in Table 4 still provide a qualitative overview of the relative hydrogen-bonding abilities of the various types of C—H donors, particularly where large numbers of potential donors are available. Thus, for the well populated C—H···O=C systems there is a remarkable consistency in the n_3/n_1 and n_4/n_1 percentages (*ca* 33 and 26%) for C—H donors arising from the three-membered rings I, II and III. These percentages fall (to 21.2 and 15.8%) for the methylene protons of (VI), perhaps due to the reduced accessibility of H (although this artefact was not further investigated). There is a further clear reduction (to 17.5 and 12.5%) in C—H···O=C contact formation for the Csp^3—H donor of (V). However, for the acetylenic protons of (VII) the n_3/n_1 and n_4/n_1 percentages are considerably enhanced by comparison with other donor C—H and for all O-acceptor subgroups. This enhancement is a

Table 5. *Mean values of geometrical parameters defined in Fig. 1 for C(ring)—H···O contacts involving rings I, II and III and the O acceptors (a) C═O, (b) C—O—H and (c) C—O—C*

Distances are in Å, angles in (°) with e.s.d.'s in parentheses.† Search criteria *A* and *B* are defined in Table 1, $N_{\rm obs}$ is the number of observations of each contact from Version 5.08 of the CSD.

Ring C—H	Criteria	$N_{\rm obs}$	d(HO)	d(CO)	ρ_H	$\lvert\theta\rvert$	$\lvert\varphi\rvert$
(*a*) For C═O acceptors							
I	*A*	410	2.65 (1)	3.54 (1)	142 (1)	36 (1)	139 (2)
	B	327	2.60 (1)	3.52 (1)	145 (1)	25 (1)	136 (2)
II	*A*	79	2.61 (2)	3.46 (2)	138 (2)	35 (2)	135 (3)
	B	63	2.56 (2)	3.46 (2)	143 (2)	32 (3)	139 (3)
III	*A*	235	2.63 (1)	3.50 (1)	140 (1)	35 (2)	139 (2)
	B	181	2.58 (1)	3.49 (1)	144 (1)	32 (2)	141 (2)
(*b*) For C—O—H acceptors							
I	*A*	34	2.80 (3)	3.62 (3)	134 (3)	29 (3)	130 (7)
	B	15	2.68 (4)	3.62 (4)	147 (3)	28 (5)	133 (9)
II	*A*	10	2.71 (5)	3.62 (6)	144 (5)	30 (7)	134 (10)
	B	8	2.66 (5)	3.59 (6)	146 (5)	33 (8)	130 (11)
III	*A*	66	2.64 (2)	3.52 (2)	141 (2)	22 (2)	131 (4)
	B	58	2.61 (2)	3.51 (2)	142 (2)	21 (2)	134 (4)
(*c*) For C—O—C acceptors							
I	*A*	29	2.66 (4)	3.55 (4)	142 (3)	14 (2)	143 (4)
	B	24	2.60 (4)	3.52 (4)	144 (3)	14 (2)	140 (5)
II	*A*	8	2.60 (5)	3.38 (6)	129 (3)	17 (3)	152 (6)
	B	6	2.58 (7)	3.41 (8)	134 (3)	15 (4)	159 (4)
III	*A*	292	2.65 (1)	3.49 (1)	138 (2)	26 (1)	140 (1)
	B	214	2.58 (1)	3.49 (1)	143 (1)	24 (1)	140 (2)

† Here, and in Table 6, the e.s.d.'s of the mean values ($\sigma_{\rm mean}$) are given in parentheses. Values of $\sigma_{\rm sample}$, which give a measure of the spread of the observations, can be obtained using $\sigma_{\rm sample} = (N_{\rm obs})^{1/2}\sigma_{\rm mean}$.

reflection of the increased acidity of Csp^1—H protons by comparison with their Csp^2—H or C(ring)—H counterparts.

In Table 4 we also present data for C—H···O═C systems that occur in CSD entries which lack any (strong) O—H or N—H donors. We denote this acceptor as C═O*, but note that the exclusion of other strong donors results in only a small percentage increase in C—H···O═C formation. By contrast, a comparison of the more highly populated subgroups of Table 4 would imply that carbonyl oxygen is a more potent acceptor of (C)H bonds than either hydroxy or ether oxygens, an observation that is well documented for stronger (N,O)—H···O systems (Jeffrey & Saenger, 1991).

3.2. *Geometrical characteristics of C(ring)—H···O systems*

Table 5 lists mean values for the geometrical descriptors of Fig. 1 for C—H donors from rings I, II and III to the O acceptors: (*a*) C═O, (*b*) C—O—H and (*c*) C—O—C. Mean values are given for both sets of constraints given in Table 1. In all subsets having a number of contributors ($N_{\rm obs}$) ≥ 50, there is a remarkable consistency in the mean values obtained for the different systems. Mean values of d(HO) at 2.60–2.65 Å are close to the sum of van der Waals radii [O = 1.52 Å: Bondi (1964), H = 1.10 Å: Rowland & Taylor (1996)], while mean values for the C—H···O angle (ρ_H) are predominantly in the 140–150° range.

It is possible to conjecture that changing atom X from C in (I) to the increasingly electronegative N,O in (II) and (III) might progressively increase the $\delta+$ charge on C2—H. However, that conjecture is not supported either by the *ab initio* partial charges (Table 3) or by significant and consistent foreshortenings of d(HO) and d(CO) in (I)→(III) in any of the crystallographic results cited in Table 5.

Given the geometrical similarities observed in Table 5, we have coalesced the results for rings I, II and III under a common heading, denoted as C(r)—H and, in Table 6, we compare the overall C(r)—H···O geometries for (*a*) C═O acceptors and (*b*) C—O—C,H acceptors with analogous data obtained for C(h)—H···O, where (h) indicates the formal hybridization state of C in substructures (V), (VI) and (VII). The most obvious features of Table 6 are the gradual but systematic shortenings of d(HO) and d(CO) as the C-hybridization changes from sp^3 to sp^2 to sp^1. Indeed, the latter change (from Csp^2 to Csp^1) is quite dramatic, as expected from earlier studies (Desiraju & Murty, 1987; Pedireddi & Desiraju, 1992). The mean d(HO) and d(CO) values for both C(r)—H···O systems (Table 6) are most comparable to (indeed, are slightly shorter than) the data for Csp^2—H···O systems. This result is completely consistent with the well known ethylenic nature of cyclopropane and with the use of $\sim$C$sp^{2.2}$ hybrids by

Table 6. *Comparison of mean values of geometrical parameters defined in Fig. 1 for C—H···O contacts involving the donors: C(r)—H from all three-membered rings (I, II and III), Csp^3—H from V, Csp^2—H from VI and Csp^1—H from VII*

Separate mean values are given for (*a*) carbonyl >C=O acceptors and (*b*) ether/hydroxy C—O—C,H acceptors. Geometrical search criteria *B* (Table 1) were used throughout. Distances are in Å and angles are in (°) with e.s.d.'s in parentheses (see footnote to Table 5). N_{obs} is the number of observations in each case from Version 5.09 of the CSD. Also tabulated are *n*(vdW), the percentage of the *d*(HO) contacts that are less than the sum of van der Waals radii (2.62 Å, see text), and *r*, the correlation coefficient that links ρ_H and *d*(OH).

Donor	N_{obs}	*d*(OH)	*d*(CO)	ρ_H	$\lvert\theta\rvert$	$\lvert\varphi\rvert$	*n*(vdW)	*r*
(*a*) C=O acceptors								
C(*r*)—H	577	2.59 (1)	3.50 (1)	145 (1)	33 (1)	141 (1)	56.5	−0.385
C*sp*^{3}—H	740	2.67 (1)	3.57 (1)	143 (1)	36 (1)	140 (1)	36.4	−0.320
C*sp*^{2}—H	296	2.62 (1)	3.56 (1)	147 (1)	33 (1)	136 (2)	48.0	−0.365
C*sp*^{1}—H	29	2.30 (4)	3.31 (3)	157 (3)	23 (3)	139 (4)	89.7	−0.646
(*b*) C—O—C,H acceptors								
C(*r*)—H	540	2.61 (1)	3.52 (1)	144 (1)	21 (1)	138 (1)	51.5	−0.300
C*sp*^{3}—H	704	2.68 (1)	3.60 (1)	145 (1)	23 (1)	138 (1)	30.0	−0.292
C*sp*^{2}—H	208	2.65 (1)	3.58 (1)	146 (1)	23 (1)	135 (2)	40.9	−0.243
C*sp*^{1}—H	40	2.43 (4)	3.39 (3)	151 (2)	20 (2)	142 (4)	75.0	−0.613

C(*r*) in exocyclic bond formation (see *Introduction*). Further, the *d*(CO) values obtained for C(*r*)—H···O systems, taken together with available (Pellerite & Brauman, 1980) pK_a values [in $(CH_3)_2SO$: pK_a = 28 for cyanocyclopropane; pK_a = 23 for benzenesulfonylcyclopropane], fit well into the *d*(CO) *versus* pK_a plot presented by Pedireddi & Desiraju (1992) and which constitutes a crystallographic scale of carbon acidity.

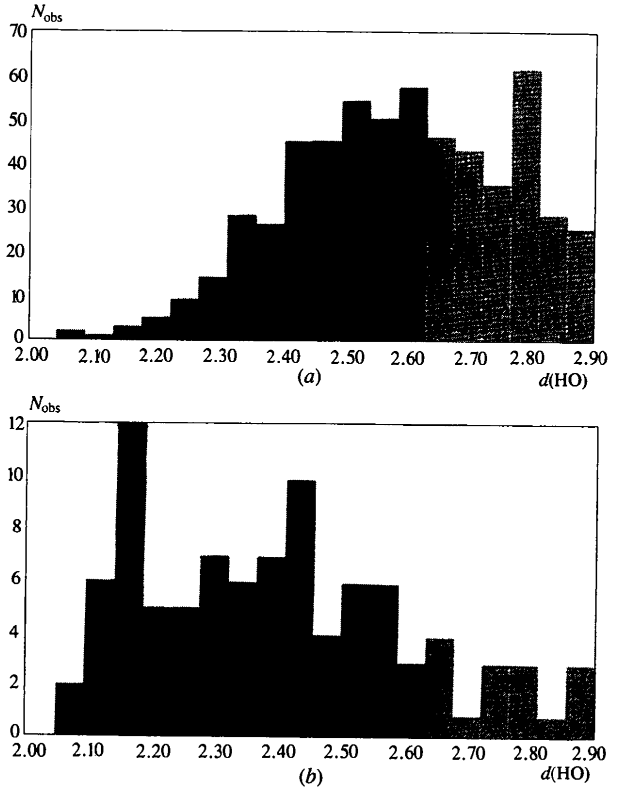


Fig. 2. Comparative histograms of the hydrogen bond length *d*(HO) in Å: (*a*) for C(ring)—H donors and (*b*) for C*sp*^{1}—H donors. Values of *d*(HO) ≤ 2.62 Å are filled in for both plots.

The variations in length (strength) of the C—H···O bonds in Table 6 are also consistent with variations in the residual positive charge on H in the various systems. Table 3 shows residual charges of +0.11 (C*sp*^{3}—H in propane), +0.127 (C*sp*^{2}—H in ethylene) and a dramatic increase to +0.233 e (C*sp*^{1}—H in acetylene) that mirrors the significant foreshortening of *d*(HO) and *d*(CO) (Table 6) for C*sp*^{1}—H···O systems. Partial charges for C(*r*)—H are in the range 0.123–0.139 e, entirely consistent with the geometrical data of Table 6. The increasing strength of the C—H···O bonds as C(*h*) changes from *sp*^{3} to *sp*^{1} is also clearly apparent from the *n*(vdW) values (vdW = van der Waals) of Table 6. This parameter is the percentage of *d*(HO) ≤ 2.62 Å, the sum of van der Waals radii, and follows the expected ordering C*sp*^{3} < C*sp*^{2} < C(*r*) ≪ C*sp*^{1}. Fig. 2 shows histograms of *d*(HO) for bonds formed by (*a*) C(*r*)—H and (*b*) C*sp*^{1}—H to any oxygen acceptor. Values of *d*(OH) ≤ 2.62 Å are shaded in both histograms.

Small differences do exist between the *d*(HO) values for C=O and C—O—C,H acceptors (Table 6). The mean ⟨*d*(HO)⟩ for the ether oxygen case are all longer than the comparable means for carbonyl oxygen. Despite being statistically marginal, these differences are consistent with their known comparative acceptor abilities (=O > —O—, see Jeffrey & Saenger, 1991). In general, C—H···O hydrogen-bond lengths are less sensitive to O-basicity than they are to H-acidity. However, even here, systematic trends are discernable (Steiner, 1994), with very delicate effects revealed when the sampling of crystallographic data is sufficiently large (Braga, Grepioni, Biradha, Pedireddi & Desiraju, 1995).

Other features of the C—H···O geometries (Table 6) are also of interest. Thus, the mean C—H···O angles (ρ_H) are consistently in the range 140–150° for C(*r*), Csp^3 and Csp^2 donors. This angle increases significantly, however, for the Csp^1 donor and for both acceptors. This tendency for the shorter (stronger) hydrogen bonds to become more nearly linear ($\rho_H \rightarrow 180°$) is well known and is exemplified in Fig. 3, which shows scatterplots of d(HO) *versus* ρ_H: (*a*) for all C(*r*)—H···O and (*b*) for all Csp^1—H···O hydrogen bonds. Regression lines are included on both plots and a considerably higher correlation coefficient, $r[d(\mathrm{OH}),\rho_H] = -0.343$ (*a*) *versus* -0.630 (*b*) is obtained for the Csp^1—H donor. Correlation coefficients for individual systems are included in Table 6.

The directionality of the H···O bonds is also summarized in Table 6 by mean values of $|\theta|$ and $|\varphi|$ (Figs. 1*b* and *c*). For both acceptors, values of $|\theta|$ and $|\varphi|$ close to 0 and 120°, respectively, indicate close alignment of the H···O vector with the conventionally viewed oxygen lone-pair direction. Here, the mean $|\theta|$ values are consistently higher than for, say, O—H···O situations. However, $\langle|\theta|\rangle$ for ether oxygens are significantly lower than for carbonyl oxygens, where $\langle|\theta|\rangle$ only falls below 30° for the stronger Csp^1—H···O bonds. The $\langle|\varphi|\rangle$ values are remarkably consistent across all subgroups of Table 6. The mean is considerably higher than the expectation value (120°), but is consistent with comparable data for N,O—H···O=C systems (Taylor, Kennard & Versichel, 1984; Allen, Bird & Rowland, 1996).

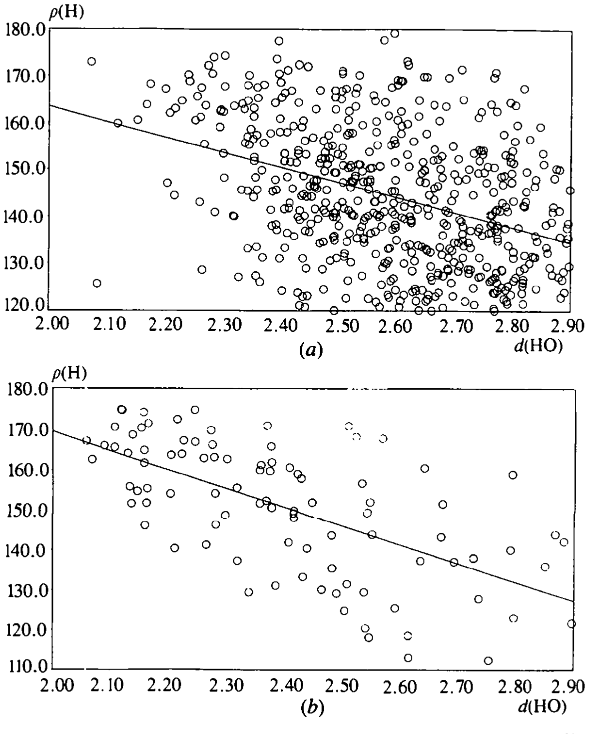


Fig. 3. Comparative scatterplots, with least-squares regression lines included, of d(HO) in Å *versus* the hydrogen-bond angle (ρ_H) in °: (*a*) for C(ring)—H donors and (*b*) for Csp^1—H donors.

Table 7. *Geometry of C—H···X (X=N,O) hydrogen bonds formed by cyclopropene H atoms*

The distances d(HX) and d(CX) (Fig. 1) are in Å and the angle ρ_H (Fig. 1) in °. E.s.d.'s are 0.01-0.02 Å for d(HX), 0.008-0.01 Å for d(CX) and 0.8-2.4° for ρ_H. Atomic nomenclature is given in (IV). R is the crystallographic residual.

Refcode	R	Acceptor (X)	d(HX)	d(CX)	ρ_H
(*a*) C1—H donors					
PSMCPR[a]	0.078	O(S=O)	2.75	3.00	92
PSMCPR[a]	0.078	O(S=O)	2.68	3.17	107
(*b*) C2—H donors					
GATXEE[b]	0.054	O(C=O)	2.31	3.28	148
GIDHUW[c]	0.052	N(>N)	2.38	3.36	151
TANHAR[d]	0.046	O(NO$_2$)	2.66	3.42	126
TANHAR[d]	0.046	O(NO$_2$)	2.83	3.17	98
TMSOCO[e]	0.037	O(C=O)	2.40	3.42	158

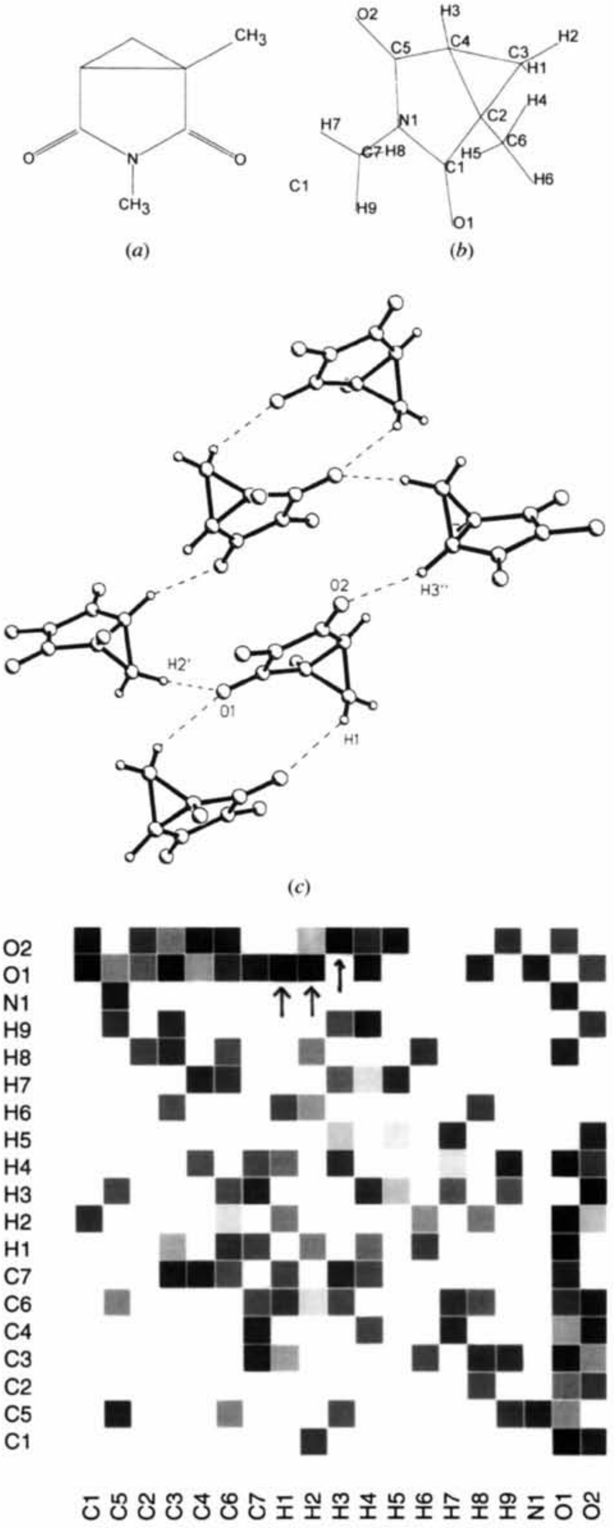
(*a*) Beckhaus, Kimura, Watson, Venier & Kojic-Projic (1979); (*b*) Baird, Hussein & Clegg (1988); (*c*) Schollkopf, Hupfeld, Kuper, Egert & Dyrbusch (1988); (*d*) O'Bannon, Carroll & Dailey (1991); (*e*) Frei, Schweizer, Wolf & Jeger (1979).

3.3. *Hydrogen-bond donor properties of cyclopropene H atoms*

The CSD contains 46 examples of (IV) in 43 entries that pass the secondary search criteria noted in the *Methodology*. This sample includes ten benzocyclopropenes, none of which contain C1—H atoms and potential hydrogen-bond acceptors. Of the remaining 36 rings with localized (C2=C2′) double bonds, six contain a C1—H and a potential acceptor and four have an available C2—H and a potential acceptor. Relevant hydrogen-bond geometry, on a structure by structure basis and located using criteria *A* of Table 1, are presented in Table 7.

Only one of the six possible C1—H (formally Csp^3—H) atoms forms hydrogen bonds (PSMCPR, Table 7). Both of these bonds are long and have poor C—H···O geometry. We note that the residual charge on C1—H in (IV) is lower than for C—H in (I)-(III) (Table 1) and that other potential H-donors exist in the structures of (IV).

The situation for the highly acidic C2—H is, however, very different. Here, the C-hybrid used in exocyclic bond formation has acetylenic properties ($\sim sp^{1.2}$; Allen, 1982*b*) and the residual charge of +0.158 e on C2—H in (IV) is higher than for C(*r*)—H or for Csp^2—H (see Table 3). All four of the structures of (IV) identified above form C2—H···X hydrogen bonds. The two bonds formed to nitro O atoms (TANHAR; Table 7) are long and show poor linearity (ρ_H). The other three bonds, however, show typical hydrogen-bond



(a) (b)

(c)

(d)

Fig. 4. C(ring)—H···O=C< bonds in CSD refcode EACLID: (*a*) 2D chemical formula, (*b*) 3D structure with atomic nomenclature, (*c*) section of crystal packing plot and (*d*) the NIPMAT matrix of short non-bonded contacts (see text).

geometry. The two bonds to carbonyl O atoms (GATXEE, TMSOCO; Table 7) show *d*(HO) distances that are slightly longer than for Csp^1—H···O=C systems (Table 6), but very significantly shorter than those involving C(*r*)—H or Csp^2—H donors. It appears that C2—H in cyclopropene is a potent C—H donor, a result that is entirely consistent with the acetylenic properties of the double bond in (IV) (Closs, 1966).

3.4. *The structural significance of C(ring)—H···O bonds*

In the vast majority of cases, the C(ring)—H···O bonds occur as secondary hydrogen bonds in the presence of much stronger bonds involving O—H or N—H donors. This secondary nature of C—H···O bonds is noted elsewhere (Desiraju, 1991; Jeffrey & Saenger, 1991). In some cases, however, C—H are the only donors in the presence of strong acceptors such as >C=O and C—H···O bonds which assume a greater significance in molecular assembly. To test this hypothesis, a search of the CSD was carried out for structures that contained: (*a*) only C, H and O, (*b*) a cyclopropane ring with at least one available C—H donor, (*c*) a >C=O acceptor and (*d*) did *not* contain a divalent oxygen, —O—, in any form. A total of 52 structures contained 182 available C(ring)—H donors and 80>C=O acceptors. A total of 55 C(ring)—H···O hydrogen bonds were located in this subset using geometrical criteria *B* of Table 1. Here, the percentage of potential donor-H that form hydrogen bonds, 30.2%, is only marginally greater than for the general case of hydrogen-bond formation by (I), 26.1% for criteria *B* (Table 4). However, the ratio of hydrogen bonds (55) to the number of available acceptors (80) is now 68.8%, much higher than the ratio (327:785 = 41.7%) in the general case (see Table 4) for criteria *B*.

We have examined the non-bonded contacts formed in some of these structures and find that, where there is a choice of C—H donor to >C=O, it is invariably C(ring)—H···O that form the shortest contacts, *i.e.* they can be regarded as primary and structure determining non-covalent interactions. A typical example is (1*S*,2*R*)-*N*-methyl-1-methyl-1,2-cyclopropanedicarboximide (CSD refcode EACLID: Polonski, Milewska & Katrusiak, 1993). The 2D (two-dimensional) chemical formula and 3D structure (with atomic nomenclature) is shown in Figs. 4(*a*) and (*b*). The crystal packing (Fig. 4*c*) is dominated by C(ring)—H···O=C< interactions: (*a*) a cyclic tetrameric unit is formed around the centre of symmetry at 0.5,0.5,0.5 ($P2_1/c$) *via* pairs of intermolecular O1···H2 and O2···H3 bonds of length 2.27 and 2.37 Å, respectively (normalized H-positions), and (*b*) a pair of O1···H1 bonds (2.48 Å) form a dimeric unit about the symmetry centre at 1,0,0. Thus, all three of the available C(ring)—H are involved in the overall scheme.

In Fig. 4(*d*) we show the non-bonded interaction pattern matrix (NIPMAT: Rowland, 1994, 1995; Rowland & Bugg, 1996). This visual representation of crystal packing is based on the 'normalization' of intermolecular distances (d_{ij}) *via* d_{ij}(normalized) = $d_{ij} - v_i - v_j$, where v_i and v_j are van der Waals radii (Bondi, 1964) for element types *i* and *j*. The d_{ij} used are the *shortest* contacts made by atoms (*i*) of a reference molecule to atoms *j* (= 1 to *i*) of neighbouring molecules. This yields a square ($i \times i$) matrix of d_{ij} values that are symmetric about the leading diagonal. When re-expressed as d_{ij}(norm) values on a van der Waals radius 'scale', the matrix elements are shaded from black [d_{ij}(norm) < −1.0 Å] to white [d_{ij}(norm) > 1.0 Å]. The NIPMAT for EACLID (Fig. 4*d*) shows quite clearly that the O1 and O2 contacts (arrowed) to the three available cyclopropane H atoms, H1, H2 and H3, are the shortest (most heavily shaded) non-bonded contacts in the extended crystal structure.

4. O,N—H···π Hydrogen bonding to three-membered rings

4.1. *Geometrical search and data analysis*

The two modes of *X*—H···π (ring) bonding (VIII*a*,*b*) suggested by Joris, Schleyer & Gleiter (1968) were examined using the 3D substructure search of Fig. 5. Here, the primary constraint for the *QUEST3D* non-bonded search is the 3.0 Å limit on the distance from (normalized) H to the C1—C2 midpoint (*X*1). The search is designed to locate both edge-on (VIII*a*) and face-on (VIII*b*) contacts (and any possible intermediate geometries) *via* an additional constraint on the angle *a*(H*X*1*Y*) of Fig. 5. As the H atom moves from edge-on to face-on, this angle decreases from an optimum 180° to a value of approximately 80° when H overlies *X*2 (using 1.5 Å as the ring edge length and 2.5 Å as the H···*X*2 distance for face-on contacts). In practice, we need to allow a reasonable tolerance below 80° to capture all relevant contacts in the search. However, this tolerance cannot be too large, else *X*—H···*Y* hydrogen bonds to rings having *Y* = N or O will then be picked up. After some experimentation, *a*(H*X*1*Y*) was constrained to lie between 45 and 180° and *d*(H*Y*) was required to be greater than 2.4 Å. Under these conditions, contacts *X*—H···*Y* represent very poor hydrogen-bonding geometries and *d*(H*Y*) is either equal to or greater than the face-on contact distance *d*(H*X*2).

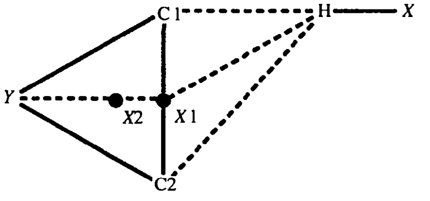


Fig. 5. Non-bonded 3D substructure search for O,N—H···π(ring) contacts. Points *X*1 and *X*2 are, respectively, the midpoint of the C1—C2 bond and the centroid of the C1—C2—*Y* ring. Element *X* was permitted to be N or O only, element *Y* was C, N or O. Geometrical search constraints are discussed in the text.

The 3D substructure of Fig. 5 was located 41 times in 32 CSD entries that also conformed to the standard secondary search criteria described in *Methodology*. Of these hits, 21 represent intramolecular contacts and 20 are intermolecular. Cyclopropane is the dominant π-acceptor (30 instances), followed by oxirane (seven instances) and aziridine (four instances). The predominant *X*—H donor is oxygen (31 instances) with 10 instances of nitrogen donors.

The scatterplot of *d*(H*Y*) *versus* *a*(H*X*1*Y*) (Fig. 6) is highly revealing. The linear plot (correlation coefficient 0.945) shows three discrete clusters of observations: (*a*) a cluster with *a*(H*X*1*Y*) tending towards 180° and with the longest *d*(H*Y*) values, (*b*) a cluster with *a*(H*X*1*Y*) less than 90° and having the shortest *d*(H*Y*) values and cluster (*c*) of five observations with intermediate *d*(H*Y*) values and *a*(H*X*1*Y*) in the range 100–120°. Fig. 6, which essentially maps the position of donor-H with respect to the rings, is entirely consistent with the *X*—H···π (ring) interaction models proposed by Joris, Schleyer & Gleiter (1968) from their spectroscopic data. Cluster (*a*) represents edge-on contacts to a ring bond with H in the plane of the ring (VIII*a*). As the H rises from the ring plane, the small cluster (*c*) is observed, which may be regarded as containing geometrically distorted variants of the edge-on geometry. Finally, as the donor-H moves above the

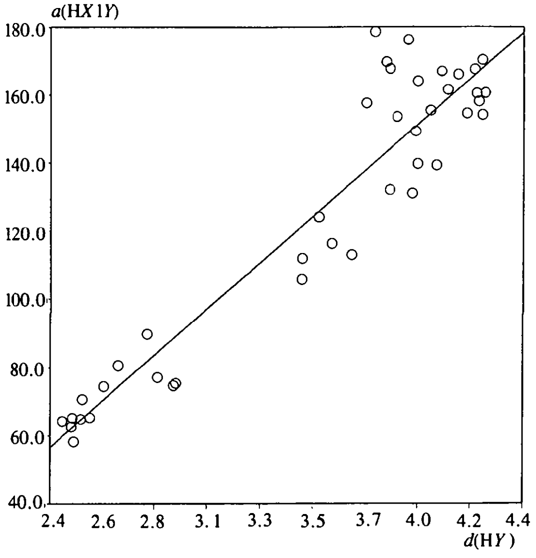


Fig. 6. Plot of *d*(H*Y*) in Å *versus* *a*(H*X*1*Y*) in ° for hits from the search illustrated in Fig. 5.

Table 8. *Mean geometry for* X—$H\cdots\pi$*(ring) interactions for rings I, II and III*

With reference to Fig. 5 and (VIII), parameters for 'edge-on' contacts are $d = \mathrm{H}\cdots X1$ distances; $\theta_1 = \mathrm{H}\cdots X1\cdots Y$ angle; θ_2 = larger angle $\mathrm{H}\cdots X1$—C1,2; θ_3 = smaller angle $\mathrm{H}\cdots X1$—C1,2. For 'face-on' contacts, $d = \mathrm{H}\cdots X2$ distance; θ_1, θ_2 and θ_3 are, respectively, the largest, intermediate and smallest of the $\mathrm{H}\cdots X2\cdots$ ring atom angles. Distances are in Å, angles in °, with e.s.d.'s in parentheses. The total number of observations (N_{obs}) in each subgroup is given, together with the numbers of contributors that have Y = C,N or O and X = N or O as designated in Fig. 5. The numbers of intra- (n_1) and intermolecular (n_2) contacts are also given for each subgroup.

	Edge-on		
	Main group	Intermediate	Face-on
d	2.81 (4)	2.82 (5)	2.68 (4)
θ_1	158 (3)	114 (3)	111 (3)
θ_2	102 (2)	102 (5)	84 (1)
θ_3	78 (2)	78 (5)	76 (2)
N_{obs}	23	5	13
Y = C (I)	16	3	11
Y = N (II)	2	1	1
Y = O (III)	5	1	1
X = N	5	2	3
X = O	18	3	10
n_1	9	3	9
n_2	14	2	4

ring, we reach cluster (*b*), which has the 'face-on' geometry of VIII*b*.

Mean geometrical parameters for the two major clusters (*a*) and (*b*), and for the minor cluster (*c*), are collected in Table 8. If we describe the three-membered rings in this study as equilateral triangles of edge length 1.5 Å (a valid description in view of the dominance of cyclopropane in Table 8) and use the mean values of 2.81 and 2.69 Å of $\mathrm{H}\cdots X1$ and $\mathrm{H}\cdots X2$, respectively, as representative of symmetric edge-on (planar) and face-on (perpendicular) geometries, then we obtain idealized (equal) H···C distances of 2.91 Å for the edge-on geometry and 2.83 Å for the face-on geometry. Obviously, some asymmetry does occur, as evidenced by the deviation of mean θ values (Table 8) from their ideal values of 180 and 90°. Nevertheless, the H···C distances cited above are comparable to H···C distances cited by Viswamitra, Radhakrishnan, Bandekar & Desiraju (1993) for N,O—H···π bonds to acetylenes, ethylenic double bonds and phenyl rings, and by Steiner (1995*a*,*b*) for C≡C—H···π(C≡C) and π(phenyl) systems.

4.2. *Examples of O—H···π(cp) hydrogen bonding*

As with the C(ring)—H···O bonds, the N,O—H···π(ring) bonds are secondary to much stronger formal hydrogen bonds. Fig. 7(*a*) shows a typical intramolecular edge-on O—H···π(cp) bond in CSD entry HNOBCH (House, McDaniel, Sieloff & VanDerveer, 1978). Here H1 is also involved in a normal O1—H1···O2=C hydrogen bond that is the dominant intermolecular feature. Nevertheless, H1 is almost coplanar with the cyclopropane ring C1, C2 and C3 and almost equidistant from C2 and C3, with H1···C1 > 3.3 Å. The CSD entry KAXTOS (Weber, Hecker, Csoregh & Czugler, 1989) provides an example of an intramolecular face-on bond (Fig. 7*b*). Again the carboxylic acid groups are involved in extensive intermolecular hydrogen bonding (not shown), but the carboxyl hydrogen is positioned under the cp ring so as to form a strong intramolecular O—H···O=C bond *and* be approximately equidistant from the three cp C atoms (2.50–3.00 Å) with an H2···cp(centroid) distance of 2.60 Å.

At the intermolecular level, the most interesting structure is SEJFIW (Schreiber, Smith & Schulte, 1989), which shows (Fig. 7*c*) both intermolecular edge-on *and* face-on O—H···π(cp) bonding, in addition to O—H···O bonds that are omitted for clarity. The edge-on C—H14 contacts yield an H14···C—C(midpoint) distance of 2.87 Å. This is one of the 'intermediate' contacts of Table 8 with H14 almost above the coordinated C5—C6 bond with an angle H14···C—C(midpoint)···C4 of 106° and H14···C4 = 3.46 Å. By contrast, H7···C(cp) contacts are much shorter (2.47–2.76 Å) with an H7···cp(centroid) distance of 2.54 Å. Taken together, the O—H···π(cp) bonds in SEJFIW appear to provide significant secondary stabilization of the extended structure.

5. Conclusions

This study provides clear evidence for the formation of C—H···O (particularly C—H···O=C) hydrogen bonds in which the donor proton is attached to a saturated three-membered carbocyclic or heterocyclic (N,O) ring. The comparative geometrical data, together with the relative frequencies of hydrogen-bond formation, would indicate a hydrogen-bond strength ordering of $\mathrm{C}sp^1$—H···O > C(ring)—H···O $\simeq$ $\mathrm{C}sp^2$—H···O > $\mathrm{C}sp^3$—H···O. Such an ordering is in excellent agreement with the known ethylenic properties of the C(ring) proton, including $\mathrm{p}K_{\mathrm{a}}$ values and partial charges from *ab initio* calculations, that result from the C-hybridizations adopted in these strained rings. Despite the small number of examples, there is evidence to suggest that cyclopropene C=C—H protons are relatively potent hydrogen-bond donors, generating C=C—H···O bonds that approach the strength of $\mathrm{C}sp^1$—H···O bonds. Again, this is a consequence of the C-hybridizations in cyclopropene which imbue the C=C—H protons with a high $\delta+$ charge.

The study also provides, for the first time, experimental confirmation of the existence of O or N—H···π(three-membered ring) bonds, as proposed almost 30 years ago from spectroscopic data (Joris, Schleyer & Gleiter, 1968). The work presented here

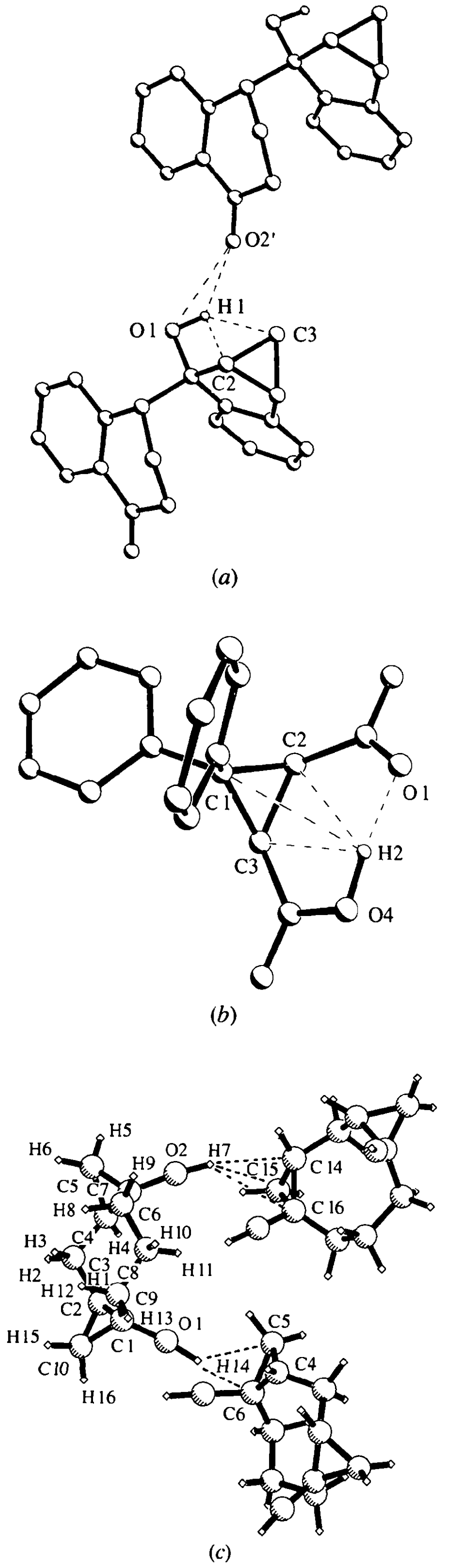


Fig. 7. Examples of O—H···π(cp) hydrogen bonds: (*a*) intramolecular edge-on bonding in HNOBCH, (*b*) intramolecular face-on bonding in KAXTOS and (*c*) intermolecular edge-on and face-on contacts in SEJFIW.

clearly shows that the two modes of H···π(ring) bonding (edge-on and face-on H-approach) suggested on the basis of the spectroscopic and chemical data of 1968 are, indeed, the major bonding modes observable in the available crystallographic data. More extensive *ab initio* calculations are now being planned to try to establish the strengths of these novel O,N—H···π(ring) bonds.

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