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The Geometry of Small Rings. VII.* Geometric Variations in Bicyclo[1.1.0]butane: Comparison with Higher Bicyclo[*n*.1.0]alkanes (*n* = 2–4)

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Abstract

The molecular geometry obtained by X-ray methods for 22 derivatives of bicyclo[1.1.0]butane (I) has been analysed in conjunction with relevant microwave results. Substructure (I) exists in a variety of environments, classified here in terms of the number of atoms (t) which bridge the 2,4-methylenes and the number (r) which bridge the 1,3-methines (*i.e.* [*r*.1.1]propellanes). Parent (I) has $t = r = 0$ and the lengths of the 1–3 bridge and 1–2 side bonds are identical [$d_{13} = 1{\cdot}497\,(3)$, $d_{12} = 1{\cdot}498\,(4)$ Å: Cox, Harmony, Nelson & Wiberg (1969). *J. Chem. Phys.* **50**, 1976–1980]; the dihedral angle between cyclopropyl rings (φ) is $121{\cdot}7\,(5)°$ and the bridgehead-substituent valence angle (ρ) is $128{\cdot}4\,(3)°$. In 2,4-bridged derivatives φ is constrained to decrease as t decreases from 3 to 1. For non-propellanes ($r = 0$) this produces synchronized geometric distortions: d_{13} decreases [to $1{\cdot}408\,(3)$ Å at $\varphi = 94{\cdot}1\,(2)°$] while d_{12} and ρ both increase. This inter-dependence is examined here by simple- and multiple-regression techniques: the positive linear correlation of d_{13} with φ has >99·5% significance, the negative d_{13}–ρ correlation is >98% significant. These systematic geometric variations are augmented by non-systematic effects induced by 1,3- or 2,4-π-acceptor substituents, indicative of the appreciable π character in the 1–3 bond. The [*r*.1.1]propellanes have highly inverted C(1,3) tetrahedra and bonding effects do not follow the trends for $r = 0$ structures. A comparison of (I) with higher bicyclo[*n*.1.0]alkanes ($n = 2$–4) shows clear correlations of geometry with strain energies and NMR coupling constants.

Introduction

Bicyclo[*n*.1.0]alkanes (Table 1, I–IV for $n = 1$–4) are strained systems characterized by cyclopropane fusion to a carbocycle of size $n+2$. The total strain energy (E_s, Table 1) in these bicyclic systems increases rapidly with decreasing n, and for (II)–(IV) E_s approximates $\sum E_s$ for the two component rings [VIII + (V–VII)]. For bicyclobutane (I) E_s exceeds $\sum E_s$ for two cyclopropane rings by ~42 kJ mol^{-1} (superstrain), and the molecule exhibits a range of unusual properties in comparison to the more normal (III) and (IV) (Wiberg, 1968*a*; Greenberg & Liebman, 1978). The characteristics of bicyclopentane (II) lie between these two extremes, a fact which is not readily deduced from total E_s values.

The NMR coupling constants $^1J_{\rm CH}$ in Table 1 show that the bridgehead methine proton in (III) and (IV) is cyclopropane-like (*i.e.* ethylenic, see VIII, IX). $^1J_{\rm CH}$ then increases through (II) to an acetylenic (acidic) value of 202 Hz in (I), close to the 220 Hz for the

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* Part VI: Allen (1984).

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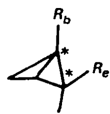
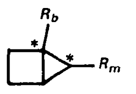
Table 1. *Strain energies* (E_s, kJ mol^{-1}), ^{13}C–H *spin–spin coupling constants* ($^1J_{CH}$, Hz) *and* C*–R *bond lengths* [d_{CH}, d_{CC} *in* Å *for* R = H, C(sp^3)] *for bicyclo*[*n*.1.0]*alkanes* (I–IV, *n* = 1–4) *and related hydrocarbons*



(I)



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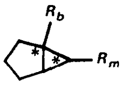

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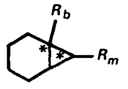
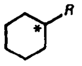
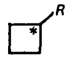


(IV)

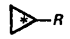


(V)

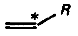
(VI)



(VII)



(VIII)



(IX)

(X)

(XI)

Compound	E_s[a]	E_s(CH$_2$)[b]	E_s(CH)[c]		$^1J_{CH}$	(% *s*)[d]	d_{CH}[e]	d_{CC}	(% *s*)[f]
V	5·9	0·8	—		125[g]	(25)	1·116 (4)[n]	1·538 (1)[v]	(23)
VI	30·5	6·3	—		128[g]	(26)	1·114 (2)[o]	1·538 (1)[v]	(23)
VII	114·6	28·9	—		134[g]	(27)	1·092 (10)[p]	1·528 (1)[w]	(27)
VIII	118·4	39·3	—		160[g]	(32)	1·089 (3)[q]	1·519 (2)[v]	(31)
IX	—	—	—		159[h]	(32)	1·083 (5)[r]	1·510 (2)[w]	(34)
IV	126·8	4 × 0·8	42·3	*b*	160[i]	(32)	—	1·516 (3)[x]	(32)
		1 × 39·3		*m*	—	—	—	1·519 (4)[x]	(31)
III	141·8	3 × 6·3	41·8	*b*	169[j]	(34)	—	1·508 (6)[x]	(35)
		1 × 39·3		*m*	159[j]	(32)	—	1·521 (5)[x]	(30)
II	239·7	2 × 28·9	71·5	*b*	178[k]	(36)	1·082 (3)[s]	1·501 (5)[x]	(38)
		1 × 39·3		*m*	—	—	1·089 (3)[s]	—	—
I	278·2	2 × 39·3	100·0	*b*	202[l]	(40)	1·074 (4)[t]	1·499 (5)[x]	(39)
				exo	152[l]	(30)	1·089 (4)[t]	1·520 (2)[x]	(31)
				endo	170[l]	(34)			
X	228·0	1 × 39·3	94·6	*b*	220[m]	(44)	1·072 (1)[u]	1·477 (6)[y]	(46)
				m	172[m]	(34)	1·088 (2)[u]	—	—
XI	—	—	—		250[h]	(50)	1·059 (–)[r]	1·464 (2)[v,w]	(50)

Notes and references: (*a*) Total strain energy, values from Greenberg & Liebman (1978). (*b*) Strain energy per methylene = E_s/n for monocycle of size *n*. (*c*) Strain energy per methine CH = $0{\cdot}5[E_s - \sum E_s(\mathrm{CH_2})]$. (*d*) *s* character of C* hybrid calculated from % $s = 0{\cdot}20\ ^1J_{CH}$ (Muller & Pritchard, 1959*a*, *b*). (*e*) From electron diffraction (ED) and microwave (MW) results. (*f*) X-ray results, % *s* for C* hybrid calculated from $r_h(= d_{CC} - 0{\cdot}769) = 0{\cdot}408 \log(\%\ p)$ (Allen, 1981*a*). (*g*) Aydin & Günther (1981). (*h*) Muller & Pritchard (1959*a*, *b*). (*i*) Fringuelli, Gottlieb, Hagaman, Taticchi, Wenkert & Wovkulich (1975). (*j*) Christl & Herbert (1979): data for tricyclo[3.1.1.0^{2,4}]heptane. (*k*) Bertrand, Grant, Allred, Hinshaw & Strong (1972). (*l*) Wiberg, Lampman, Ciula, Conner, Schertler & Lavanish (1965). (*m*) Closs (1966). (*n*) Ewbank, Kirsch & Schafer (1976): ED. (*o*) Adams, Geise & Bartell (1970): ED. (*p*) Almenningen, Bastiansen & Skancke (1961): ED. (*q*) Bastiansen, Fritsch & Hedberg (1964): ED. (*r*) Sutton (1965): ED. (*s*) Mathur, Harmony & Suenram (1976): MW. (*t*) Averages of MW results for (I) (Cox, Harmony, Nelson & Wiberg, 1969) and for benzvalene (Suenram & Harmony, 1973). (*u*) Stigliani, Laurie & Li (1975): MW. (*v*) Allen (1981*a*). (*w*) Allen (1984). (*x*) This work. (*y*) Allen (1982*a*).

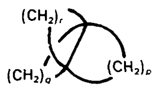
highly acidic H$_b$ in cyclopropene (X). The *s* character of the C(1,3) exocyclic hybrid therefore increases with E_s from ~32% in (IV) to ~40% in (I). The available $^1J_{CH}$ for cyclopropyl methylenes (I, III, X) fall in a narrow range (152–172 Hz) centred on the 160 Hz of free cyclopropane (VIII). This implies that CH$_2$ groups are relatively unaffected by changes in *total* E_s. Hence we may use the E_s per CH$_2$ group in the parent rings (V–VIII) to derive simple estimates of the strain-energy increment due to each bridgehead methine (Table 1). The E_s(CH) in (III), (IV) are almost identical to E_s(CH$_2$) for cyclopropane, but the increase in E_s(CH) through (II) to the maximum in (I) is clearly correlated to the bridgehead $^1J_{CH}$ values and with other chemical and physical properties of the series. The exocyclic C*–*R* distances in Table 1 all follow these trends and are fully discussed in later sections.

The above results imply bonding variations in (I)–(IV) which arise from systematic changes in hybridization at the bridgeheads, C(1,3). This is particularly exemplified in the chemistry of (I) and (II), thus: the 1–3 bridge bond in (I) exhibits considerable π character; (I) rearranges to 1,3-butadiene *via* cleavage of two side (1–2) bonds while rearrangement of (II) to cyclopentene involves only (1–3) cleavage; both molecules undergo endocyclic attack by reactive unsaturated molecules. All of these physical and chemical factors have provoked considerable theoretical interest (see *e.g.* Newton, 1977) in (I) and (II), and a brief survey of such studies serves to introduce the relevant sections below.

The chemical and theoretical work has been given a structural focus over the past decade *via* accurate microwave (MW) studies of (I) (Cox, Harmony, Nelson & Wiberg, 1969) and (II) (Suenram &

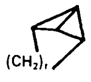
Harmony, 1972; Mathur, Harmony & Suenram, 1976), together with more than 50 X-ray, MW and electron diffraction (ED) studies of derivatives of (I)–(IV). The most interesting features of (I) are the identical bridge (1–3) and side (1–2) bond lengths: 1·497 (3) and 1·498 (4) Å respectively, and the 'inverted' bridgehead tetrahedra, *i.e.* all four interatomic vectors emanating from C(1, 3) are directed within a single hemisphere.

Interest in these highly-strained systems has received added impetus recently from chemical and structural studies of 1,3-bridged derivatives, the tricyclo[$n.m.1.0^{x,y}$]alkanes (XII, XIII), and of 2,4-bridged species such as tricyclo[$1.1.1.0^{4,5}$]pentane (XIV, $t = 1$). In (XIV) with $t = 1, 2$ the flap angle between the two cyclopropane rings is constrained to values below the 121·7° found for (I) (Cox *et al.*, 1969). Systems of general formula (XII) are better known as [*p.q.r*]propellanes and their chemistry has been extensively reviewed by Ginsburg (1975). Synthesis of the elusive [1.1.1]propellane (XIII) has recently been reported by Wiberg & Walker (1982). It has a calculated E_s of ~441 kJ mol^{-1} (Newton & Schulman, 1972*b*), which indicates superstrain of > 126 kJ mol^{-1} over $\sum E_s$ for three cyclopropane rings, and C(1,3) strain increments of ~160 kJ mol^{-1}. The [3.1.1], [4.1.1] and [3.2.1]propellanes are of particular structural interest since tetrahedral inversion, noted for (I) above, is enhanced by small-ring (1,3)-bridging. An accurate structural study of (XIII) is an ultimate goal in this area.



(XII)

(XIII)



(XIV)

In this paper the endocyclic and exocyclic geometries of (I)–(IV) and of their bridged derivatives of types (XII), (XIV) are examined and related to chemical and theoretical studies of bonding and hybridization. The analysis follows the pattern established in earlier parts of this series which dealt with the parent small-ring systems (VIII: Allen 1980, 1981*a*, *b*, 1982*a*; VII: Allen, 1984). The primary sources of data are X-ray studies retrieved from the Cambridge Structural Database (CSD) (Allen *et al.*, 1979), together with available MW and ED results.

Methodology

The April 1982 release of CSD has been used for this study, except for substructure (I) where the literature has been continuously monitored. Substructure searches, data retrieval and numerical analyses were performed using computer programs described by Allen *et al.* (1979). Searches were restricted to those compounds normally regarded as organic (CSD classes 1–61, 63, 64, 70). X-ray studies are identified throughout by CSD reference code, and short-form references are listed alphabetically by this code in Table 2.* In a few cases unpublished coordinate sets have been supplied by the authors (see Acknowledgements) and are not available in CSD; such entries are denoted by an asterisk in Table 2. Geometric tabulations refer to parameters defined in Fig. 1. For bicyclobutane (I) the nature and position of substituents is important to the discussion and chemical diagrams for these structures, together with two derivatives of (II), are presented in Fig. 2 (produced *via* the CSD Chemical Graphics System: Cartwright, Kennard & Watson, 1983). ED and MW results are assigned a suitable mnemonic (*e.g.* BCB) in the relevant table, but are cited in the normal manner *via* the table footnote.

Where mean values $\bar{x}$ are cited their e.s.d. has been calculated as $\sigma(\bar{x}) = [\sum_n (\bar{x} - x_n)^2/n(n-1)]^{1/2}$ for n

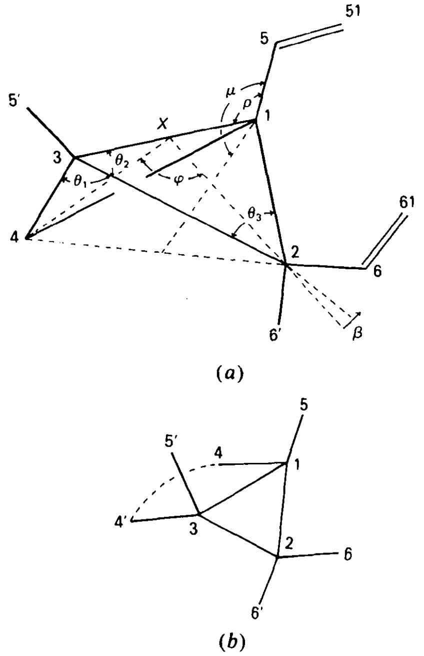


Fig. 1. (*a*) Geometric parameters used in the analysis of bicyclobutane (I). φ is the dihedral angle between the planes 1–2–3 and 1–4–3; μ is the angle between the 1–5 bond vector and the plane defined by 1, 2 and 4; β is the methylene rocking angle. For π-acceptor substituents the torsion angles used in the text are $\tau_{15} = 3–1–5–51$ and $\tau_{26} = X–2–6–61$; where X is the mid-point of the 1–3 bond and $\tau_{26} = 0°$ or $180°$ for *cis*- or *trans*-bisected conformations respectively. (*b*) Nomenclature of the bridgehead region in higher ($n = 2, 3, 4$) bicyclo[*n*.1.0]alkanes. Geometric parameters correspond to those for (I).

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* Full literature citations for these entries have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39059 (5 pp). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

independent observations $x_i(i=1-n)$. The relationship $\sigma(\text{sample})=\sqrt{n}\,\sigma(\bar{x})$ may be used to estimate the spread within any sample. Values of $\bar{x}$ are quoted as $\bar{x}(\sigma, n)$ throughout.

Bicyclo[1.1.0]butane

Molecular geometry for the bicyclobutane substructure (I) in a variety of environments is collected in Table 3. Results are averaged over C_{2v} symmetry and ordered by increasing length of the bridgehead (1–3) bond. Data for the only hetero-analogue studied so far, the 2,4-disilabicyclobutane MESIBU, are also included.

Theoretical studies

The anomalous properties of (I) were noted in the *Introduction*. Apart from very high E_s and $^1J_{\text{CH}}$ (bridgehead) values (Table 1), the compound also has a large dipole moment of $2{\cdot}252\pm0{\cdot}03\times10^{-30}$ Cm (Harmony & Cox, 1969; Cox *et al.*, 1969) and a *negative* $^1J_{\text{CC}}$ (bridge bond) coupling constant which assigns ~91% *p* character to the C(1,3) hybrids forming the 1–3 bond (Pomerantz, Fink & Gray, 1976). The significant π character of this bond is reflected in the UV spectra of 1,3-diphenyl derivatives which suggest conjugated phenyl groups (Woodward & Dalrymple, 1969). The attack by reactive unsaturated molecules from the endocyclic direction is indicative of electron deficiency in this area.

A qualitative Walsh orbital study (Pomerantz & Abrahamson, 1966) yielded two bonding models. Both indicated significant π contributions to the 1–3 bond, but neither was conducive to endocyclic attack. The prediction, in both models, that the 1–3 bond was shorter than the 1–2 side bond was not confirmed by the results for BCB (Table 3).

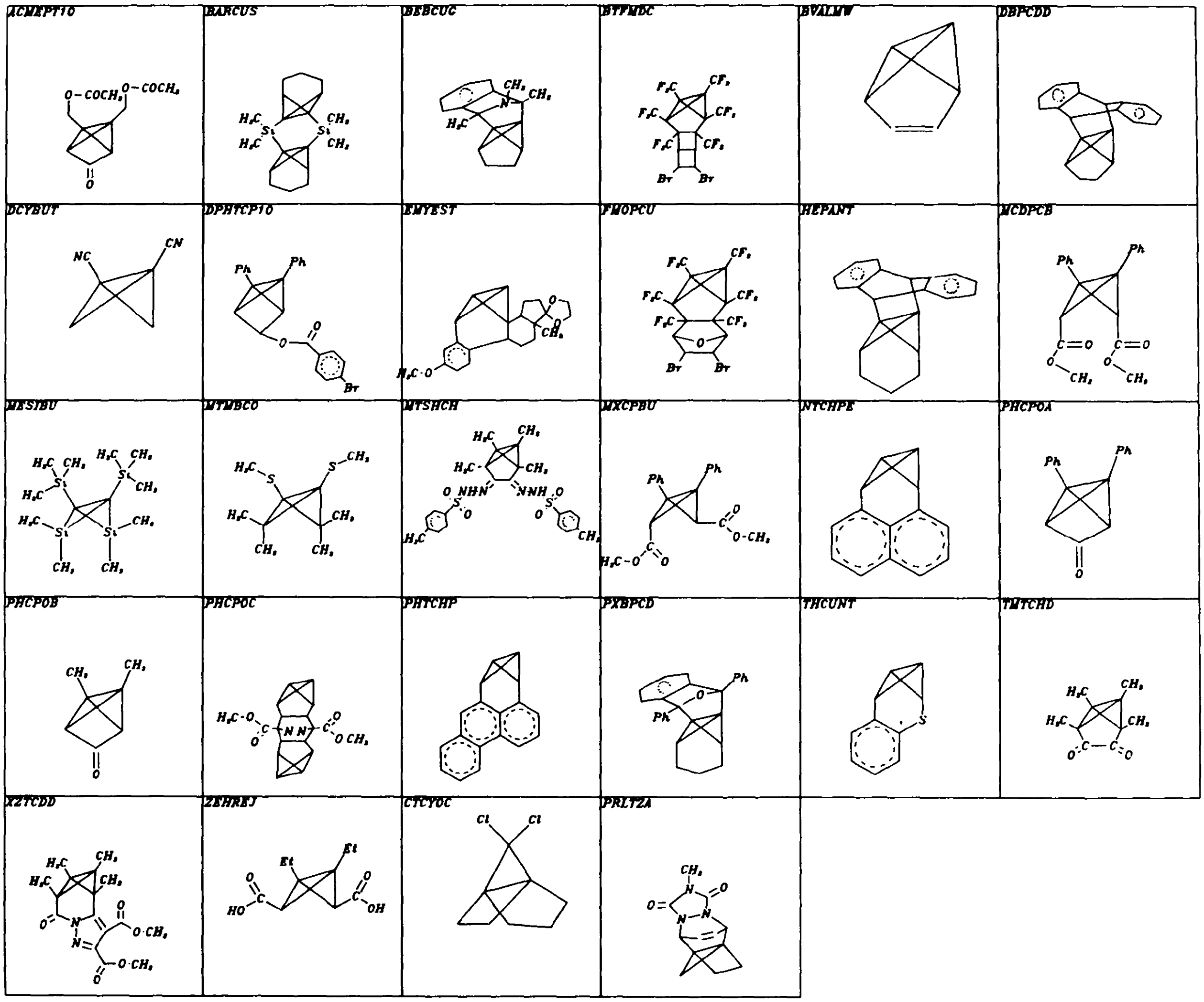


Fig. 2. Chemical structural diagrams for 26 derivatives of bicyclo[1.1.0]butane ordered alphabetically by CSD reference code. The final two compounds are propellane derivatives of bicyclo[2.1.0]pentane.

Table 2. *Short-form references to X-ray studies, ordered alphabetically by reference code*

Code	Journal	Vol.	Page	Yr
ACMEPT10	*J. Org. Chem.*	47	4240	82
AXHTUJ	*Rec. Trav. Chim. Pays-Bas*	98	52	79
AXIVAL10	*Acta Cryst. B*	29	2783	73
BARCUS	*Chem. Ber.*	114	3896	81
BEBCUG	*J. Am. Chem. Soc.*	103	7378	81
BERTPP	*Tetrahedron*	34	753	78
BTFMDC	* *Tetrahedron Lett.*		1795	77
BUPRGE10	*Bioorg. Khim.*	6	752	80
BUTLIE	*a J. Chem. Soc. Chem. Commun.*		44	73
BXTCUN	*J. Chem. Soc. Perkin*		460	76
CGRANB10	*J. Chem. Soc. B*		1079	71
CPENTS	*Chem. Ber.*	106	2883	73
CTCYOC	*J. Am. Chem. Soc.*	94	7402	72
DBPCDD	* *Angew. Chem. Int. Ed. Engl.*	17	848	78
DBTCHX	*a ACA Abstr. (Winter)*		35	69
DCYBUT	*J. Org. Chem.*	37	2762	72
DPHTCP10	*b J. Chem. Soc. A*		2027	67
EBCPUR	*J. Am. Chem. Soc.*	100	5110	78
EBHYUR	*J. Am. Chem. Soc.*	100	5110	78
EMYEST	*Helv. Chim. Acta*	55	544	72
EXPPCA	*Helv. Chim. Acta*	59	1395	76
FMOPCU	*b Tetrahedron Lett.*		2545	76
HEPANT	*Acta Cryst. B*	34	3472	78
HVERCS	*J. Chem. Soc. Perkin Trans.* 2		763	80
MCDPCB	*Cryst. Struct. Commun.*	8	135	79
MCMNON	*Rec. Trav. Chim. Pays-Bas*	98	271	79
MENTCN	*Helv. Chim. Acta*	63	1856	80
MESIBU	*Z. Anorg. Allg. Chem.*	475	87	81
MPASSF10	*J. Chem. Soc. Perkin Trans.* 2		605	77
MTMBCO	*Tetrahedron Lett.*		4457	79
MTSHCH	*Cryst. Struct. Commun.*	8	325	79
MXCPBU	*Cryst. Struct. Commun.*	8	131	79
NTCHPE	*Acta Cryst. B*	33	272	77
NVRCSN	*J. Chem. Soc. Chem. Commun.*		822	80
PHCPOA	* *Angew. Chem. Int. Ed. Engl.*	18	694	79
PHCPOB	* *Angew. Chem. Int. Ed. Engl.*	18	694	79
PHCPOB01	*Angew. Chem. Int. Ed. Eng.*	21	775	82
PHCPOC	* *Angew. Chem. Int. Ed. Engl.*	18	694	79
PHTCHP	*Acta Cryst. B*	33	2344	77
PRLTZA	*Acta Cryst. B*	36	2672	80
PXBPCD	* *Nouv. J. Chim.*	3	357	79
TCNONC	*Cryst. Struct. Commun.*	6	307	77
THCUNT	*a Angew. Chem.*	86	738	74
TMTCHD	*b Cryst. Struct. Commun.*	6	259	77
XZTCDD	*Cryst. Struct. Commun.*	7	303	78
ZEHREJ	* *Acta Cryst. B*	39	61	83

Notes: (*a*) Coordinate data not available. (*b*) Structure excluded from analysis due to low precision [geometry for DPHTCP10 is, in fact, in excellent agreement with related $t = 1$ structures (Table 3) despite the high R of 0·16 and high bond length e.s.d.'s of >0·04 Å].

* Coordinates supplied by author(s); in some cases the data have now been published.

CNDO calculations by Wiberg (1968*b*) and an *ab initio* study (Schulman & Fisanick, 1970, later elaborated by Newton & Schulman, 1972*a*) both reproduced the high dipole moment. The *ab initio* work yielded localized atomic-orbital hybridizations which are schematically depicted in Fig. 3(*a*). The 1–3 bridge bond is formed from almost pure p orbitals (sp^{24}) directed at 31° exocyclic to the bond vector; the bond has ~26% π character. The model has C(1,3) exocyclic hybrids with 39% s character, in agreement with ${}^1J_{\rm CH} = 202$ Hz (Table 1), while the side bonds are formed from sp^3 hybrids on C(1,3) and $sp^{5.1}$ hybrids on C(2,4), which are essentially cyclopropane-like. The side bonds are bent outward from the 1–2 vector by ~33° and twisted downwards into the interplanar region of (I) by ~10° at C(1,3) and ~2° at C(2,4). Similar results have also been obtained from iterative MO overlap approximations (IMOA: Maksic, Klasinc & Randic, 1966) and from NMR studies (Bertrand, Grant, Allred, Hinshaw & Strong, 1972). Recent *ab initio* SCF calculations have been performed by Skancke (1982) and by Eisenstein & Hirshfeld (1981). Charge-deformation densities derived in the latter study were clearly maximized at positions indicated by Newton & Schulman (1972*a*). Electron-density distributions from two recent X-ray analyses (PHCPOB01, ZEHREJ) have provided experimental confirmation of these models.

Energy calculations by Newton & Schulman (1972*a*) indicated low barriers for the deformation of (I) from its optimum geometry. The calculations predict changes in the length of the 1–3 bridge bond (d_{13}) resulting from changes in the interplanar angle (φ: Fig. 1*a*), and/or in the bridgehead-substituent valence angle (ρ: Fig. 1*a*). The total 1–3 overlap population increases for: (i) decreasing φ at constant ρ, and (ii) increasing ρ at constant φ. A linear decrease of d_{13} with decreasing φ was discovered by Irngartinger & Lukas (1979) using X-ray and microwave results. A more detailed *ab initio* study of these synchronized geometric distortions has been presented by Paddon-Row, Houk, Dowd, Garner & Schappert (1981).

Theoretical work on 1,3-bridged species (XII) has centred on [1.1.1]propellane (XIII). *Ab initio* studies (Newton & Schulman, 1972*b*) indicate (Fig. 3*b*) that C(1,3) forms three equivalent coplanar $sp^{1.4}$ side-bond hybrids, with a fourth sp^4 orbital perpendicular to this plane and directed outwards from the molecule (note that these hybrids are not constrained to be orthonormal). This scheme yields a negative overlap population in the 1–3 bonds, despite a predicted length of 1·60 Å. The complete absence of bonding electron density between the highly inverted (Table 3) bridgehead carbons in the [3.1.1]propellane, BEBCUG, provides verification of this model.

Experimental geometries

General features. The geometries of non-propellanes (Table 3, $r = 0$) fall into four groups which correspond to $t = 0, 1, 2, 3$ in the nomenclature of (XIV). For $t = 1, 2, 3$ the interplanar angle φ is constrained to mean values of 95·3 (6, 3), 109·3 (11, 4) and 121·3 (6, 4)°. The corresponding d_{13} values fall into discrete sequential groups with means of 1·421 (7, 4), 1·455 (3, 4) and 1·484 (9, 4) Å, providing qualitative confirmation of the expected d_{13}–φ relationship (Newton & Schulman, 1972*a*; Irngartinger & Lukas, 1979; Paddon-Row *et al.* 1981). However, the bridgehead-substituent angle (ρ) is not constant over this φ range and the predicted (Newton

Table 3. *Geometry of bicyclo*[1.1.0]*butane in a variety of environments*

Parameters are averaged over C_{2v} symmetry in the nomenclature of Fig. 1(*a*) and ordered on increasing bridgehead bond length (d_{13}). Distances in Å, angles in degrees.

Compound[a]	*R* factor	σ[b]	t[c]	r[d]	d_{13}	d_{12}	D[e]	φ	ρ[f]	μ[f]	θ_1	θ_2	θ_3	d_{15}[g]	n[h]
PHCPOB	0·046	3	1	—	1·408	1·539	1·495	94·1	144·5	197·5	81·2	62·8	54·5	1·488*	1
ACMEPT10	0·050	2	1	—	1·416	1·527	1·490	95·7	144·1	196·2	82·1	62·4	55·2	1·470*	1
PHCPOB01	0·036	—	1	—	1·417	1·545	1·502	—	—	—	—	—	—	1·484*	—
PHCPOA	0·052	3	1	—	1·443	1·526	1·498	96·2	142·1	193·4	82·0	61·8	56·4	1·453	1
BTFMDC	0·073	9	2	—	1·451	1·500	1484	109·9	138·4	184·5	91·6	61·1	57·8	1·508*	2
ZEHREJ	0·065	2	—	—	1·451	1·518	1·496	112·8	138·1	183·6	94·0	61·5	57·1	1·496*	2
BVAL(MW)[i]	—	2	2	—	1·452	1·529	1·503	106·0	133·7	181·8	89·4	61·7	56·7	—	2
MTSHCH	0·079	11	2	—	1·455	1·540	1·512	110·7	140·0	186·7	92·9	61·8	56·4	1·509*	2
PHCPOC	0·049	3	2	—	1·463	1·499	1·487	110·6	131·7*	177·2*	91·7	60·8	58·4	—	2
NTCHPE	0·060	30	3	—	1·468	1·494	1·485	120·3	127·3*	168·7*	98·1	60·6	58·9	—	–
XZTCDD	0·073	10	3	—	1·473	1·520	1·504	120·5	137·7	179·2	98·8	61·1	58·0	1·516*	3
THCUNT	0·044	5	3	—	1·483	1·487	1·486	122·0	—	—	98·8	60·2	59·7	—	3
BCB(MW)[j]	—	4	—	—	1·497	1·498	1·498	121·7	128·4	166·9	98·3	60·0	60·0	—	3
DCYBUT	0·057	6	—	—	1·503	1·483	1·490	126·4	124·6	162·1	100·6	59·6	60·9	1·424	4
EMYEST	0·074	13	3	—	1·512	1·497	1·502	122·5	121·1*	161·2*	98·3	59·7	60·7	—	3
MTMBCO	0·088	8	—	—	1·514	1·514	1·514	128·7	130·9	167·8	102·6	60·0	60·0	1·754	4
MXCPBU	0·070	20	—	—	1·516	1·522	1·520	120·6	139·6	178·7	97·8	60·2	59·7	1·473	—
DBPCDD	0·058	—	2	4	1·541	1·504	1·516	113·2	110·5	153·2	92·1	59·2	61·7	1·520*	
PXBPCD	0·047	—	3	3	1·546	1·508	1·521	121·9	102.0	141·2	97·3	59·2	61·7	1·544*	
HEPANT	0·045	5	3	4	1·549	1·516	1·527	120·7	110·3	150·0	96·7	59·3	61·4	1·540*	
BARCUS	0·071	6	3	4	1·572	1·527	1·542	118·9	122·8	163·0	95·2	59·0	62·0	1·842	
BEBCUG	0·032	2	2	3	1·573	1·512	1·532	114·3	102·4	144·1	91·7	58·7	62·7	1·539*	
MCDPCB	0·090	20	—	—	1·574	1·517	1·536	129·7	131·2	166·2	101·4	58·8	62·5	1·479	
MESIBU	0·070	15	—	—	1·781	1·838	1·819	121·9	131·3	172·4	99·7	61·0	58·0	1·847	
AVE1					1·422	1·531	1·495	95·3	143·6	195·7	81·8	62·3	55·4	1·478	
AVE2					1·454	1·517	1·496	110·0	137·7	184·9	91·9	61·4	57·3	1·504	
AVE3					1·491	1·501	1·498	121·7	133·4	173·1	98·6	60·3	59·6	1·516	
AVE4					1·509	1·500	1·503	127·6	127·8	165·0	101·6	59·8	60·5	—	

Notes: (*a*) X-ray structures with SIG > 0·03 Å are omitted. (*b*) $\sigma = \mathrm{SIG} \times 100$. (*c*) *t* is the number of atoms in 2,4-bridge (see XIV). (*d*) *r* is the number of atoms in 1,3-bridge (see XII), *i.e.* for $r \neq 0$, compounds are [*r*.1.1]propellanes. (*e*) *D* is the mean cyclopropane bond length: $D = (2d_{12} + d_{13})/3$. (*f*) * indicates values derived from X-ray determined H positions. (*g*) * indicates the substituent (5) is C(sp^3). (*h*) $n = 1, 2, 3, 4$ indicates that this structure is included in AVE*n* below. (*i*) Suenram & Harmony (1973). (*j*) Cox, Harmony, Nelson & Wiberg (1969).

& Schulman, 1972*a*; Paddon-Row *et al.*, 1981) inverse correlation of d_{13} and ρ is also apparent in Table 3.

Four of the free bicyclobutanes ($t = 0$, $r = 0$) have means for d_{13}, φ of 1·508 (5) Å, 124·4 (19)° and appear in expected positions in Table 3. Two other $t = 0$, $r = 0$ structures (ZEHREJ, MCDPCB) have d_{13} values which differ significantly from this mean, and exhibit large differences in φ and ρ. Other discrepancies, *e.g.* the significant lengthening of d_{13} in PHCPOA at $t = 1$, which occur throughout Table 3, may be ascribed to substituent effects discussed in the next section.

The side-bond length d_{12} for the non-propellanes shows an inverse correlation with d_{13}, indicative of the rehybridization at C(1,3) which results from changes in φ and ρ. This relationship yields approximately constant values of *D*, the mean cyclopropane bond length. The average *D* for $r = 0$ is 1·500 (3, 18) Å, somewhat shorter than the mean of 1·510 (1) Å for the free ring (Allen, 1980).

The inversion parameter μ [Fig. 1(*a*), Table 3] is a measure of the distortion of the C(1,3) tetrahedra. Values above 180° represent severely distorted 'normal' tetrahedra, $\mu = 180°$ implies a distorted trigonal prism with the 1–2, 1–4, 1–5 bond vectors in the equatorial plane of a sphere centred on C(1), while with $\mu < 180°$ all *bond vectors* are directed to a single hemisphere and the tetrahedron is 'inverted'. The latter situation applies to all of the free bicyclobutanes ($t = 0$, $r = 0$) and propellanes (t, $r > 0$) in Table 3, with the exception of ZEHREJ. However, this is not the point at which the bonding model changes from that in Fig. 3(*a*) to that in Fig. 3(*b*). This should be close to the point at which the tetrahedra formed by the *localized atomic orbital directions* at C(1,3) become inverted. This must occur at $\mu < 158°$, a value based on the 22° bond bending in free cyclopropane (Allen, 1982*b*), and probably at $\mu \simeq 150°$ in view of theoretical estimates of 1–2 orbital directions (Newton & Schulman, 1972*a*). The five [*r*.1.1]propellanes of Table 3, with a μ range of 163·0–141·2°, must encompass this transition point.

Effect of substituents. The d_{13} value in PHCPOA, 1·443 (3) Å, exceeds the mean d_{13} for the other $t = 1$ structures, 1·414 (3, 3) Å, by 0·029 Å or 10σ. This is a result of optimal conjugation between the 1,3-diphenyl substituents of PHCPOA [other $t = 1$ structures have C(sp^3) substituents] and the π orbitals in the bridge bond (Irngartinger & Lukas, 1979), which lie above and below the 1–3 vector in the plane bisecting the interplanar angle φ. Maximum conjugative overlap will occur when the torsion angle $|\tau_{15}|$ (Fig. 1*a*) is 90°, and the 95·2° and 90·3° observed in PCHPOA are very close to the optimal value. This conclusion is in accord with the UV spectra of Woodward & Dalrymple (1969). Such a large change in d_{13} might have been expected to produce a significant increase in φ, but this is prevented by the inflexibility of the single-atom 2,4 bridge.

In ZEHREJ both d_{13} and φ at 1·451 (2) Å and 112·8 (3)°, are smaller by $>20\sigma$ than the 1·497 (3) Å, 121·7 (5)° obtained for BCB. However, ZEHREJ has *exo,exo*-2,4-dicarboxylate substituents with each C=O π acceptor in a *cis*-bisected conformation with respect to its cyclopropane ring at τ_{26} (Fig. 1*a*) of 4·8° and −6·2°. For free cyclopropane the bisected π-acceptor conformations induce significant asymmetry in ring bond lengths (Allen, 1980): the bond opposite the substituent shortens by δ Å, the adjacent bond lengthens by $\delta/2$ Å, where δ is measured relative to the mean bond length (D) in the ring. The C=O group is a highly effective acceptor with $\delta =$ 0·026 (5) Å. In ZEHREJ the 1–3 bond, common to both rings and opposite both substituents, has $\delta =$ 0·045 Å relative to D and $\delta = 0·046$ Å relative to BCB. The additivity of asymmetries was established earlier (Allen, 1980) and the δ per C=O of 0·023 Å is close to the free ring value. Since ZEHREJ is not constrained by 2,4-bridging (*cf.* PHCPOA above) it is free to deform and φ decreases by 8·9° and ρ increases by 9·7° as d_{13} decreases.

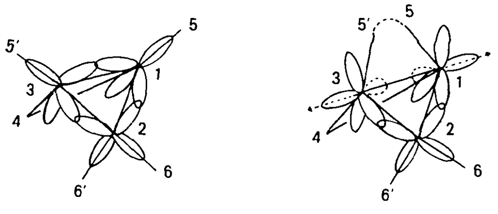
These arguments are supported by calculations by Jorgensen (1975) who showed that benzvalene (BVAL) was stabilized by electronic interaction between the 1,3 bridge and the double bond forming the 2,4 bridge. The double bond is constrained in a *cis*-bisected conformation with respect to each cyclopropane and d_{13} at 1·452 (1) Å is significantly shorter than the 1·463 (2) Å in PHCPOC, a $t = 2$ analogue with no π-acceptor substituents. However, some of this shortening must be due to the lower φ value in BVAL, and it is the increased asymmetry ($D - d_{13} = \delta = 0·051$ Å for BVAL, 0·021 Å for PHCPOC) which is, perhaps, more relevant. A similar comparison also applies to MTSHCH with 2,4-C=N substituents in *trans*-bisected positions ($\tau_{26} = -179·1°$, 176·0°); d_{13} is not significantly shorter than in PHCPOC, but asymmetry is high ($\delta = 0·057$ Å) in view of the near identity of φ values. In the $t = 3$ group XZTCDD similarly has *trans*-bisected 2,4 π acceptors ($\tau_{26} = 175·0°$ for C=O, 177·4° for C=C) and d_{13} is shorter (by 0·024 Å) than in BCB with which it shares a common φ value.

A further example of 1,3-diphenyl conjugation occurs in the unconstrained ($t = 0$) structure MCDPCB. The two phenyl groups have $\tau_{15} = 96·0°$ and 70·1° and, despite low precision, d_{13} is significantly elongated at 1·574 (20) Å relative to BCB. The ring is free to deform and φ increases by 8·0°. The effect of the 2,4-di-(C=O) substituents may be ignored here since $\tau_{26} = -46·0°$ and −67·0°. The only other compound with 1,3-diphenyl groups, MXCPBU, has unfavourable τ_{15} values of 57·7° and 61·8°; one of the 2,4-carbonyls is, however, favourably situated at $\tau_{26} = 176·0°$ and the slightly elongated d_{13} of 1·516 (20) Å may simply reflect the precision of the structure. In view of the significant effect of 1,3-diphenyl groups in favourable conformations the geometry of the 1,3-dicyano compound (DCYBUT) is somewhat surprising. The structure is well determined and there is some cyclopropyl asymmetry, but a longer d_{13} might have been expected.

The most interesting relationship links BCB, BARCUS and MESIBU. The latter has an extraordinary C–C bridge length of 1·781 (15) Å, and each C(1,3) has approximate trigonal-pyramidal geometry with three Si atoms forming the basal plane. This is precisely the situation predicted by Stohrer & Hoffmann (1972) for stabilization of trigonal-pyramidal carbon geometry: the substitution of three H atoms of CH_4 by atoms or groups with low-lying orbitals which can accept π electrons; Si is cited as a prime example. Thus in MESIBU, with three such acceptors, d_{13} elongates by 0·284 Å relative to BCB; both have $t = r = 0$ and almost identical φ values. In BARCUS each C(1,3) is bonded to only one $Si(Me)_2$ bridge and d_{13} lengthens by 0·075 Å relative to BCB. Further lengthening is restricted by structural constraints ($t =$ 3, $r = 4$) which reduce φ by ~3°; hence the value for mono-Si substitution is approaching one-third of the value for the tri-Si compound, MESIBU. The minimum μ for all three structures is 163·0°; hence implicit assumptions of the bonding model of Fig. 3(*a*) are justified.

Clear evidence is presented above for the (opposite) effects of 1,3 and 2,4 π-acceptor substituents on the length of the 1–3 bond. With the data currently available it is not possible to quantify these non-systematic effects in the presence of systematic geometric deformations caused by changes in φ and ρ. There is some evidence to suggest that the full effects of substituents in $t = 1, 2$ structures may be damped by the inflexibility of φ caused by rigid structural constraints.

Inter-dependency of geometric parameters. The predicted inter-dependency of d_{13}, φ and ρ (Newton & Schulman, 1972*a*; Paddon-Row *et al.*, 1981) is apparent by inspection of Table 3. Plots of d_{13} *vs* φ and d_{13} *vs* ρ (Fig. 4*a*, *b*) for all $r = 0$ structures indicate linear relationships, especially when low-precision data ($\sigma > 0·02$ Å) are omitted, and the slopes are in the predicted directions. To quantify the obvious



(*a*) (*b*)

Fig. 3. Schematic drawing of localized atomic-orbital directions in (*a*) bicyclobutane (I, Newton & Schulman, 1972*a*) and (*b*) [*n*.1.1] propellanes (XII, Newton & Schulman, 1972*b*); here the σ_{13} orbital points outwards along 1–3 vector, and the back lobes are shown as broken lines.

Table 4. *Results of regression analyses*

d_{13}^{11} and d_{13}^{10} are recalculated from multiple regressions of d_{13} on φ and ρ based on 11 and 10 data points [equations (1) and (2) respectively in the text], d_{13}^{φ} and d_{13}^{ρ} are from single regression of d_{13} on φ and ρ separately, based on 10 data points. An asterisk indicates a point not included in the regression.

	Observed values			Regression values (Å)			
Code	φ^0	ρ^0	d_{13} (Å)	d_{13}^{11}	d_{13}^{10}	d_{13}^{φ}	d_{13}^{ρ}
PHCPOB	94·1	144·5	1·408	1·415	1·409	1·408	1·421
ACMEPT10	95·7	144·1	1·416	1·418	1·413	1·413	1·423
PHCPOA	96·2	142·1	1·443	1·423	1·417*	1·414*	1·433*
BTFMDC	109·9	138·4	1·451	1·455	1·453	1·454	1·451
ZEHREJ	112·8	138·1	1·451	1·460	1·459	1·462	1·452
BVAL(MW)	106·0	133·7	1·452	1·455	1·451	1·443	1·473
MTSHCH	110·7	140·0	1·455	1·453	1·452	1·456	1·443
XZTCDD	120·5	137·7	1·473	1·475	1·473	1·485	1·454
BCB(MW)	121·7	128·4	1·497	1·493	1·493	1·488	1·499
DCYBUT	126·4	124·6	1·503	1·509	1·509	1·502	1·517
MTMBCO	128·7	130·9	1·514	1·502	1·505	1·508	1·487
Sample variance (V)$\times 10^5$				10·90	3·48	6·03	26·13

dependence of d_{13} on both ρ and φ a multiple-regression procedure was used, based on eleven $r=0$ structures (identified in Table 4). X-ray structures where ρ was determined from H-atom positions were omitted, as well as low-precision data ($\sigma >$ 0·02 Å); $\sigma_{\max}$ for the eleven structures was 0·011 Å in MTSHCH. The resulting equation, of the form $d_{13} = a + b_1\varphi + b_2\rho$, gave:

$$d_{13}^{11} = 1\cdot4875 + 0\cdot001850\varphi - 0\cdot001708\rho. \qquad (1)$$

The signs of b_1, b_2 imply the expected positive correlation between d_{13} and φ, and the negative correlation between d_{13} and ρ. The significance of b_1, b_2 was examined *via* the Student t test: linearity of the d_{13}–φ relationship is significant at >99·5% level (one-tailed probability), linearity of d_{13}–ρ is slighly less significant at ~95%. Values of d_{13}^{11} were computed from φ, ρ using equation (1) (Table 4) and the largest discrepancy, d_{13}^{obs}–d_{13}^{11}, occurs for PHCPOA where the predicted value is shorter than the observed value by 0·020 Å. This is precisely the structure identified above as having the least flexibility ($t = 1$) to allow a φ increase to match the significant substituent-induced lengthening of d_{13}. In contrast the $t=0$ structure ZEHREJ is well fitted by equation (1). With PHCPOA omitted the regression of d_{13} on φ and ρ was repeated for ten contributors to give:

$$d_{13}^{10} = 1\cdot4083 + 0\cdot00224\varphi - 0\cdot001447\rho. \qquad (2)$$

Predicted d_{13}^{10} values (Table 4) show a maximum discrepancy from d_{13}^{obs} of 0·009 Å and the sample variance is much lower than for d_{13}^{11}. Linearities are now ~99·9% significant for d_{13}–φ and >98% significant for d_{13}–ρ. The correlation coefficients $C(r,\varphi) = 0\cdot98$, $C(r,\rho) = 0\cdot90$ and $C(\varphi,\rho) = -0\cdot84$ show the synchronized nature of the distortions in the senses predicted by Paddon-Row *et al.* (1981).

The straight lines shown in Fig. 4(a, b) represent simple regressions of d_{13} on φ and ρ respectively, based on the ten points used to derive equation (2). Values of $d_{13}^{\varphi}(=1\cdot1364 + 0\cdot002890\varphi$; Table 4) fit d_{13}^{obs} with some accuracy and confirm the validity of the original observations of Irngartinger & Lukas (1979) based on five structures only. The d_{13}–ρ relationship is less well fitted and the sample variance for $d_{13}^{\rho}(=2\cdot1198 - 0\cdot004835\rho$; Table 4) is high. Thus, with the data currently available, equation (2) yields the best estimate of d_{13} for a given φ and ρ for structures having the bonding model of Fig. 3(a). The [r.1.1]propellanes appear to behave in an entirely different manner and are discussed separately below.

Exocyclic bonding. There are 30 independent exocyclic C(2,4)–C(sp^3) bonds in the structures of Table 3. Omission of one anomalous value (1·569 Å) in DBPCDD yields a mean of 1·521 (2, 29) Å for a range of 1·497–1·546 Å. This is virtually identical with the mean of 1·519 (2, 146) Å established for free cyclopropane (Allen, 1981a). The mean value for non-propellanes ($r = 0$) is 1·518 (3, 18) Å, within 3σ of the propellane ($r \neq 0$) value of 1·526 (3, 11) Å. The NMR data of Table 1 predict higher s character,

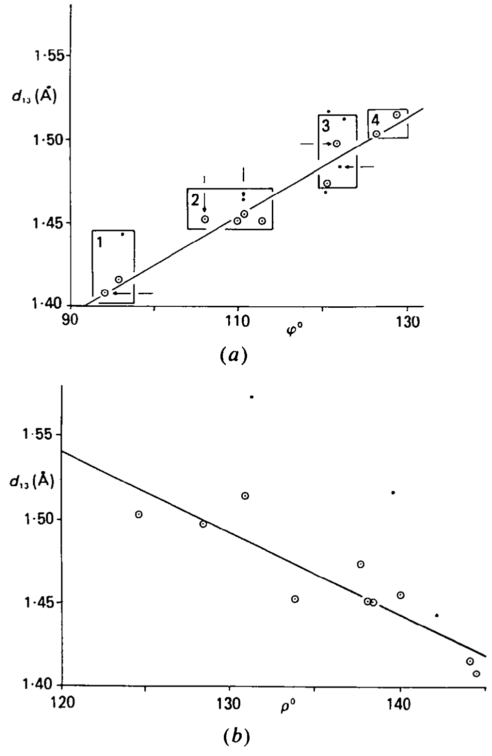


Fig. 4. (a) Plot of bridgehead bond length (d_{13}, Å) *vs* interplanar angle (φ^0) for bicylobutane (I). The ten circled points contributed to the final multiple regression of d_{13} on φ and ρ; the straight line shown is the result of a simple d_{13}–φ regression (see text) based on these ten points. The five points used by Irngartinger & Lukas (1979) are arrowed. The points within boxes n = 1–4 were used to obtain AVEn values in Table 3. (b) Plot of bridgehead bond length (d_{13}, Å) *vs* the bridgehead-substituent valence angle (ρ^0). The ten circled points contributed to the final multiple regression; the straight line shown results from a simple d_{13}–ρ regression (see text) based on these ten points.

hence shorter bonds, for the hybrid orbital directed towards *endo* substituents. This is not reflected in the X-ray data where the reverse situation is indicated: for C(sp^3) substituents $d(exo) = 1{\cdot}514\,(3, 11)$, $d(endo) = 1{\cdot}526(3, 18)$ Å.

The cyclopropane-like nature of the methylene groups in (I) is therefore clearly apparent from the X-ray data, in agreement with other experimental (Table 1) and theoretical results. The exocyclic covalent radius (r_h) for C(2,4) based on the overall mean cited above is (Allen, 1981*a*) 1·521–0·769 = 0·752 Å which corresponds, on a purely empirical basis, to an *s* character of ~30% for σ_{26} of Fig. 3(*a*). Hence the σ_{21} orbital contributes ~20% *s* to the ring σ-framework. These estimates apply to both non-propellanes and to propellanes.

The free bicyclobutanes ($t = 0$, $r = 0$) of Table 3 provide few data with which to study the methylene tilt (or rocking) angle (β in Fig. 1*a*). An NMR study (Meiboom & Snyder, 1977) gave $\beta = 1{\cdot}4°$ in the sense shown in Fig. 1(*a*), *i.e.* the C(2,4) methylenes are tilted away from each other and from the intra-annular area. An *ab initio* geometry optimization (Hehre & Pople, 1975) gave $\beta = 2{\cdot}2°$. This direction of tilt is the reverse of that observed for the unbridged parent cyclobutane; an NMR study of (VII) (Meiboom & Snyder, 1970) gave $\beta \sim -4°$ inwards towards the ring centre for puckered cyclobutane. Values of β from X-ray studies of (VII) (Allen, 1984) change systematically from 0° for the planar form to 4·3° at a puckering angle of 28·9° (equivalent to $\varphi = 151{\cdot}1°$ in I). The direction of tilt in (VII) is that required to further relieve H···H non-bonded interactions at vicinal carbons, in addition to relief produced by ring puckering. In bicyclobutane (I) vicinal interactions are minimal by comparison with transannular methylene repulsion at φ values of ~120°, hence the reversal of the tilt direction. The value of β obtained for BCB (Cox *et al.*, 1969) is −0·65°, *i.e.* not in the expected sense, but the magnitude is comparable to the error limits cited. In the X-ray studies of Table 3 only EMYEST and MTMBCO have C(2,4) which are disubstituted by non-H atoms. The three independent β values (0·9°, 4·3°, 5·9°, mean = 3·7°) are all in the expected (outward) sense, but the significance is limited.

There are 24 independent methine C(1,3)–C(sp^3) bonds in 11 structures of Table 3. For the non-propellanes ($r = 0$, $\sigma_{\max} = 0{\cdot}011$ Å) values of d_{15} (Fig. 1) range from 1·467 to 1·530 Å, with a mean of 1·499 (5, 14) Å. The C(1,3) exocyclic covalent radius is then 0·730 Å, considerably shorter than the C(2,4) methylene value determined above. The empirical X-ray estimate (Allen, 1981*a*) of *s* character is ~39% for σ_{15} of Fig. 3(*a*), close to the NMR value of ~40% for $^1J_{\rm CH} = 202$ Hz in (I) (Table 1). However, Table 3 shows some correlation of d_{15} with both φ and ρ, which is best seen in the AVE*n* (*n* = 1–4) values (Table 3); these averages are taken over structures with common φ and are shown boxed in Fig. 4(*a*). Despite the paucity of data d_{15} at $t = 1$ is consistently low for three high-precision studies. The mean value (AVE1) at 1·478 (4, 4) Å gives $r_h = 0{\cdot}709$ Å, or ~45% *s* for σ_{15}, which should be compared with $^1J_{\rm CH} = 212$ Hz (~42·5% *s*) at $t = 1$ (Closs & Larrabee, 1965). The longer d_{15} values for AVE2, 3 indicate decreasing exocyclic *s* character which follow, but exaggerate, the NMR trend of decreasing $^1J_{\rm CH}$: 206 Hz at $t = 2$, 200 Hz at $t = 3$ (Closs & Closs, 1963; Closs & Larrabee, 1965). Considerably more d_{15} values are needed to follow up these potentially interesting correlations, which offer an explanation of the wide d_{15} range exhibited in Table 3.

The propellanes ($r \neq 0$, Table 3) show significantly longer d_{15} values than those discussed above. With one anomalously short value omitted (1·475 Å in DBPCDD) a range of 1·510 to 1·564 Å yields a mean of 1·539 (5, 9) Å. This exceeds the mean for non-propellanes by ~0·04 Å (8σ) and is now identical to a normal C(sp^3)–C(sp^3) distance. The C(1,3)–C(sp^3) bonds in propellanes all form part of a five- or six-membered ring often in quite crowded situations. These constraints must lead to increased non-bonded interactions which will tend to lengthen d_{15}; nevertheless electronic factors are also implicated and these are discussed in the next section.

The acceptable correlation of exocyclic covalent radii for both methylene C(2,4) and methine C(1,3) with $^1J_{\rm CH}$ values makes it tempting to estimate the % *s* character in the 1–3 bridgehead bond in parent (I) using available X-ray evidence. This can only be done in the most approximate way by the following argument: (i) In the formalism of Fig. 3(*a*) we assume that $s_{15} + s_{13} + 2s_{12} = 100\%$. (ii) s_{15} is ~39% from the C(1,3) exocyclic radius, hence to obtain s_{13} we need an estimate of s_{12}. (iii) The C(2,4) methylenes are cyclopropane-like and contribute ~20% *s* to the σ-framework (s_{21}). (iv) The 1–2 side bond for non-propellanes with $t = 3$ or $t = 0$ is 1·501 Å, some 0·01 Å shorter than in cyclopropane itself; this shortening must be due to increased *s* character (>20%) in σ_{12}. In two X-ray studies of the spirocyclopentane substructure (Prangé, Pascard, De Meijere, Behrens, Barnier & Conia, 1980; Seebach, Dammann, Lindner & Kitschke, 1979) the cyclopropane ring bonds emanating from the spiro centre average to 1·50 (1) Å. Since this symmetric spiro centre must use sp^3 hybrids to form ring bonds, we have a parallel to the situation in (I). Thus σ_{12} may be assumed to have ~25% *s* character. The resultant estimate for s_{13} is therefore *ca* 11%, consistent with the calculations of Newton & Schulman (1972*a*).

The propellanes. The discussion above has been primarily concerned with the larger group of non-propellanes ($r = 0$, Table 3). If the relationship noted earlier between BARCUS, BCB and MESIBU is con-

Table 5. *Geometry of bicyclo*[2.1.0]*pentane in the nomenclature of Fig.* 1(*b*)

Parameters are averaged over C_s symmetry and ordered by increasing bridgehead bond length (d_{13}). Distances are in Å, angles in degrees.

Compound	R	σ	d_{13}	d_{12}	d_{14}	$d_{44'}$	D(cp)[a]	D(cp)[a]	φ	ρ[b]	μ[b]
MCMNON[c]	0·043	5	1·527	1·500	1·527	1·545	1·509	1·532	112·4	130·2	195·2
EXPPCA[c]	0·070	8	1·530	1·532	1·540	1·576	1·531	1·547	110·1	134·6	199·7
CPENTS[c]	0·064	8	1·533	1·480	1·517	1·549	1·500	1·529	112·2	124·0*	190·9*
BCP(MW)[d]	—	3	1·536	1·507	1·528	1·565	1·517	1·539	112·7	128·6	—
PRLTZA(1)	0·054	4	1·537	1·495	1·536	1·546	1·509	1·539	114·4	110·2	173·5
(2)	0·054	4	1·538	1·502	1·538	1·542	1·514	1·539	115·2	110·2	173·2
EBCPUR[c]	0·044	6	1·538	1·495	1·522	1·569	1·509	1·538	115·0	131·7*	199·0*
CTCYOC	0·065	12	1·572	1·458	1·525	1·512	1·496	1·534	113·7	108·3	170·3
X-ray mean values			1·532	1·502	1·526	1·560	1·512	1·536	112·4	132·4	197·5
(σ, n) of X-ray mean			(2, 4)	(8, 8)	(5, 8)	(7, 4)	—	—	(5, 4)	(22, 2)	(22, 2)

Notes: (*a*) D(cp) is the mean cyclopropyl bond length, D(cb) the mean cyclobutyl bond length. (*b*) Values marked with an asterisk are derived from X-ray determined H positions. (*c*) Included in X-ray average. (*d*) Suenram & Harmony (1972); Mathur, Harmony & Suenram (1976).

sidered together with the high μ (163·0°) in BARCUS, then only four structures with $r \neq 0$ (*i.e.* DBPCDD, PXBPCD, HEPANT and BEBCUG) are likely to adopt the schematic bonding model of Fig. 3(*b*). A number of geometrical factors support this view: (i) the maximum value of μ is 153·2° in DBPCDD; (ii) the d_{13} are poorly fitted by equation (2) above, the mean discrepancy $d_{13}^{\text{obs}}-d_{13}^{10}$ is 0·037 Å; (iii) the mean exocyclic d_{15}, at 1·539 (5, 9) Å, is very significantly longer than for non-propellanes. While non-bonded repulsion may be a contributory factor in this elongation, it is likely that electronic effects are predominant: the elongation implies that the orbitals σ_{15}, σ_{12}, σ_{14} are approaching equality of s character, in agreement with the theoretical predictions for (XIII) (Newton & Schulman, 1972*b*).

A regression of d_{13} on φ and ρ for the four propellanes gave $d_{13} = 1{\cdot}9154 - 0{\cdot}001346\varphi - 0{\cdot}001931\rho$, but the signs of the coefficients were not significant in a t test with only one degree of freedom. Nevertheless all d_{13} values recalculated to within 0·009 Å of their observed values, and the predicted d_{13} for (XIII) ($\varphi = 120°$, $\rho = 60°$) is 1·638 Å, consistent with the 1·600 Å predicted by the *ab initio* study (Newton & Schulman, 1972*b*).

Bicyclo[2.1.0]pentane

Available geometric data for bicyclopentanes (II) are collected in Table 5, averaged over C_s symmetry and ordered on increasing d_{13} (Fig. 1*b*). A number of structures with 2,4-bridging by one or two atoms only are omitted: one-atom bridging results in two 'bridgehead' bonds, while two-atom bridging produces a 'hybrid' which includes both substructures (II) and (III). Such structures are often further bridged, leading to bonding which is unrepresentative of the target (II). Thus Table 6 contains four X-ray studies of derivatives of (II), an accurate MW study of the parent system (BCP), a [3.2.1]propellane (CTCYOC) and a [4.2.1]propellane (PRLTZA, two molecules per asymmetric unit). An ED study of (II) (Bohn & Tai, 1970) yielded anomalous d_{13}, d_{45} values of 1·437 and 1·620 Å and is not included here.

Table 6. *Mean X-ray geometry for the bridgehead regions of bicyclo*[3.1.0]*hexane* (III) *and bicyclo*[4.1.0]*heptane* (IV) *in the nomenclature of Fig.* 1(*b*)

The microwave results for (I) (BCB, Table 3) and (II) (BCP, Table 5) are also included. Distances are in Å, angles in degrees.

	(I)	(II)	(III)[a]	(IV)[b]
d_{13}	1·497 (3)	1·536 (4)	1·517 (3)	1·519 (6)
d_{12}	1·498 (3)	1·507 (4)	1·501 (5)	1·502 (4)
d_{14}	1·498 (3)	1·528 (6)	1·521 (5)	1·523 (4)
D(cp)[c]	1·498	1·517	1·506	1·508
$D(r)$[c]	1·498	1·539	1·523	1·531
φ	121·7 (5)	112·7 (4)	114·6 (7)	109·7 (9)
ρ	128·4 (2)	128·6 (3)	121·1 (10)	116·8 (10)
d_{15}[d]	1·499 (5)	1·501 (5)	1·508 (6)	1·516 (3)
d_{26}[d]	1·521 (2)	—	1·521 (5)	1·519 (4)

Notes: (*a*) From reference codes BUPRGE10, EBHYUR, MENTCN, TCNONC. (*b*) From reference codes AXHTUJ, AXIVAL10, BERTPP, BXTCUN, CGRANB10, HVERCS, MPASSF10, NVRCSN. (*c*) D(cp) is the mean bond length in the three-membered ring, $D(r)$ is the mean bond length in the larger ring. Means are taken over non-equivalent bonds, hence no σ is given. (*d*) X-ray values for C(sp^3) substituents, see Table 1 for C–H in (I), (II).

A wide range of theoretical studies of (II) are reviewed by Newton (1977), and other *ab initio* studies have recently been published (Van Alsenoy, Scarsdale & Schafer, 1981; Skancke, 1982; Wiberg & Wendoloski, 1982). By comparison with bicyclobutane the 1–3 bond in (II) is less bent and has significantly more s character; nevertheless an appreciable π contribution still remains. The exocyclic C(1,3) hybrids in (II) are now predicted to have 37% s character ($\sim sp^{1\cdot7}$), in accord with the lower $^1J_{\text{CH}}$ of 178 Hz (Table 1), but the cyclopropyl and cyclobutyl methylenes have similar hybridizations to those found in the parent rings. An NMR study (Bertrand, Grant, Allred, Hinshaw & Strong, 1972) gives s_{xy} values for the four non-equivalent C(1,3) hybrids [see Fig. 3(*a*) where σ_{14} is now directed towards a cyclobutyl methylene and is not equivalent to σ_{12}] as $s_{15} = 36$, $s_{12} = 19$, $s_{14} = 29$ and $s_{13} = 16\%$.

The mean X-ray geometry for examples of (II) which are unperturbed by further strained bridges is given in Table 5; all mean values are within 2σ of the microwave geometry. With the data presently available it is reasonable to accept the results for BCP as definitive for (II). In these examples φ and ρ (except for propellanes) are consistent, with φ some 9° lower than in BCB (Table 3), and μ always exceeds 190°. The [4.2.1]propellane (PRLTZA) does have slight (~7°) inversion of the C(1,3) bond-vector tetrahedra, but apart from a small increase of 2·4° in φ, the framework bond lengths are unaffected by the constrained ρ values of 110·2°. In CTCYOC the [3.3.1]propellane framework is severely affected by π-donor (dichloro) substitution of the C(2) methylene. The resultant effects on bonding are fully discussed in the structural paper.

There are only seven C(1,3)–C(sp^3) bonds in the structures of Table 5, including four in the [4.2.1]propellane PRLTZA. Their mean of 1·501 (5, 7) Å is almost identical to the 1·499 (5, 11) Å obtained for (I) above. The NMR data of Table 1 would indicate that the former is shorter and the latter is longer than might have been expected from the $^1J_{\rm CH}$ values. Thus the s character of σ_{15} in (II) is ~38% from the X-ray data.

A comparison of the microwave geometries for (I) (BCB, Table 3) and (II) (BCP, Table 5) shows that the cyclopropyl side bond (d_{12}) in (II) is elongated, and is now close to the free-ring value. This suggests a reduction in s character of σ_{21} (Fig. 3a) to the ~20% which is normal in the free ring. The cyclobutyl side bond (d_{14}) in (II) is short at 1·528 (3) Å (MW) or 1·526 (5) Å (X-ray), when compared with values in excess of 1·55 Å in planar cyclobutane itself (Allen, 1984). In the free ring (VII) bond lengths are affected by non-bonded repulsions across each bond between eclipsed vicinal substituents, and by transannular C–C repulsion across the ring. Both of these effects are apparent in $d_{44'}$, where the microwave and X-ray values are quite normal. However, for the 1–4 side-bond, vicinal repulsions are significantly reduced by cyclopropane fusion, and this must contribute to the shortening of d_{14}. But it is unlikely that steric effects are wholly responsible for the ~0·035 Å difference between d_{14} and $d_{44'}$. It is therefore probable that the s character of the σ_{14} orbital in (II) is somewhat greater than the 23% in free cyclobutane (Allen, 1984), as suggested by the NMR results of Bertrand *et al.* (1972), which gives $\sigma_{14} = 29\%$ s.

The bridge bond (d_{13}) in (II) at 1·536 (3) Å in BCP (Table 5) is 0·04 Å longer than in (I) (BCB, Table 3). Results obtained for free cyclobutane (Allen, 1984) would indicate that 0·02–0·03 Å of this increase is due to non-bonded repulsion effects in planar (VII). Thus the internuclear 1–3 distance corrected for these effects is approximately the normal value for free cyclopropane.

Higher bicycloalkanes

There are numerous examples of cyclopropane fusion to five- and six-membered rings in CSD. However, a high proportion of these contain point(s) of unsaturation in the larger ring, or are further fused or bridged in ways which bring additional strain to the system. These structures have been avoided, as have structures where the cyclopropyl methylene is substituted by π donors, or by π acceptors which are in conjugative conformations (Allen, 1980); both types of substituents would lead to unrepresentative geometry. With these restrictions, and a requirement of $R < 0{\cdot}10$, only four derivatives of bicyclo[3.1.0]hexane (III) and eight of bicyclo[4.1.0]heptane (IV) remained for analysis.

The mean X-ray geometries for the bridgehead regions of (III) and (IV) are in Table 6, where the definitive MW results for (I) and (II) are also included. ED results for (III) (Mastryukov, Osina, Vilkov & Hilderbrandt, 1977) give an anomalous bridge bond of 1·454 (9) Å, reminiscent of a similar ED anomaly for (II) (Bohn & Tai, 1970). This reflects the problems involved in resolving a single peak, which represents a mean C–C distance, into its closely related constituent parts. In contrast the MW study of bicyclo[3.1.0]hexan-3-one (Bevan, Legon, Ljunggren & Mjoberg, 1978) has $d_{13} = 1{\cdot}519\ (1)$, $d_{12} = 1{\cdot}510\ (3)$ Å and $\varphi = 113{\cdot}1\ (3)$°, consistent with the X-ray means for (III).

In (III) and (IV) the cyclopropyl bonding approaches that in the free ring. The d_{26} values (Table 6) are identical to the free-ring value of 1·519 (2, 146) Å (Allen, 1981a) and confirm the cyclopropane-like nature of the C(2) methylenes throughout the series. The effects of increased fused-ring size are, however, most apparent at the bridgehead C(1,3) atoms. Thus the s character of the exocyclic hybrid continues to decrease from the ~39% in (I) through 38% in (II) to values of 35% in (III) and 33% in (IV) (obtained from d_{15} as described above). Values of ρ in (III) and (IV) also decrease, as expected, with decreasing % s. Thus the lengths of the two bonds at C(1,3) which are exocyclic to the three-membered ring (d_{15},d_{14}, see Fig. 1b) are nearly identical in (IV), *i.e.* C(1,3) now exhibit the properties of free-ring methylenes. The mean endocyclic cyclopropane bond lengths [D(cp), Table 6] for (III) and (IV) are also close to the 1·510 (2) Å obtained for the free ring (Allen, 1980). There is, however, some asymmetry in the individual distances with $d_{13} > d_{12}$. The elongation of d_{13} may be ascribed partly to eclipsed non-bonded interactions between atoms 4,4′ of Fig. 1(b), which are brought closer together by the constraints of ring fusion, and partly to slightly unequal s characters in the relevant C(1,3) hybrids, σ_{12}, σ_{13}.

Discussion

The observed geometries of (I)–(IV) are consistent with the *ab initio* results for this series (Newton, 1977).

The relative strength of the 1–3 bond in (I), especially at lower φ values, is in accord with its preservation during thermal ring opening to 1,3-butadiene; thermolysis of (II) and (III) involves 1–3 bond cleavage (Wiberg, 1968*a*). The appreciable π character of the 1–3 bond in (I), so evident in its chemistry, is reflected in the bond-length elongation induced by conjugative interactions with 1,3-diphenyl substituents. Interactions between the endocyclic nucleus of (I) and 2,4 π-acceptor substituents is also apparent and is deserving of further structural study. The energetic ease of distortion of (I), together with the synchronized nature of these distortions (Newton & Schulman, 1972*a*; Paddon-Row *et al.*, 1981), has been noted in previous structural studies (particularly PHCPOB, ZEHREJ). The distortions have been studied here by application of multiple-regression methods; such techniques will be more effective when a larger data set is available.

The results of this analysis also show that the molecular geometries of bicyclo[*n*.1.0]alkanes follow the trends indicated by variations in strain energies and NMR coupling constants (Table 1). The C*–C(sp^3) distances of Table 1, established from X-ray results both here and in earlier parts of this series (references in Table 1), are particularly well correlated with $^1J_{\rm CH}$ values, as illustrated in Fig. 5. For the present study the decreasing acidity of the 1,3 protons in (I)–(IV) is clearly seen, in contrast to the constant characteristics of the C(2) methylenes ($^1J_{\rm CH} \sim 160$ Hz, $d_{\rm CC} \sim 1{\cdot}52$ Å) throughout the series. With the straight line drawn between two major reference points, 1·538 Å at $^1J_{\rm CH} = 125$ Hz (C* = sp^3) and 1·464 Å at $^1J_{\rm CH} = 250$ Hz (C* = sp), the probable underestimation of d_{15} in (II) and its overestimation in (I) is highlighted. The graph would indicate d_{15} values of ~1·493 Å for (I) and ~1·505 Å for (II); more accurate X-ray results are required to confirm these predictions.

In earlier parts of this series (Allen 1981*a*, 1982*a*, *b*, 1984) and in the present work it has proved useful to convert the effective covalent radii (r_h) for C* atoms in Table 1 to an approximate % *s* character. This approximation has been effected by a simple empirical expression (Allen, 1981*a*). The % *s* character used in exocyclic-bond formation by *e.g.* (I)–(IV), (VII), (VIII), (IX) (Table 1) has provided some insight into the endocyclic bonding in strained small-ring systems. In particular, it has provided a simple framework with which to relate the experimental X-ray results to other experimental and theoretical data. This is otherwise difficult to achieve since the endocyclic C–C distances in strained systems cannot be directly compared with their unstrained counterparts. During this work it has been found that the empirical X-ray estimates of *s* character are directly correlated with those predicted by $^1J_{\rm CH}$ values, at least for the range of compounds included in Table 1 and Fig. 5. The relationship between $^1J_{\rm CH}$ and % *s* was first proposed (Muller & Pritchard 1959*a*, *b*) on a purely empirical basis. However, there is now a body of evidence (Ellis & Ditchfield, 1976, and references therein) which indicates that the relationship has a sound theoretical basis for many hydrocarbons, including a range of small-ring compounds (Ellis & Ditchfield, 1976; Newton, Schulman & McManus, 1974; Ellis & Maciel, 1970).

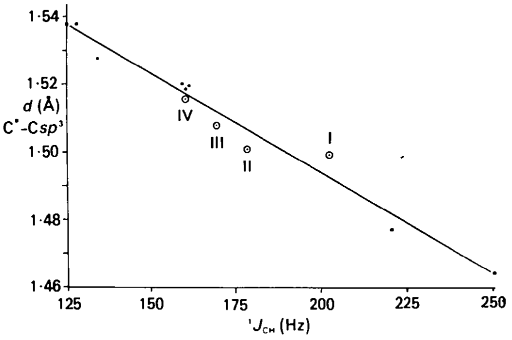


Fig. 5. Plot of exocyclic C*–C(sp^3) bond lengths (*d*, Å) *vs* NMR spin–spin coupling constants ($^1J_{\rm CH}$, Hz) listed in Table 1. The bridgehead-substituent distances for (I)–(IV) are identified.

For these reasons the results of Fig. 5 have some more general implications. They suggest that small electronic variations and redistributions do leave their trace in the *average* molecular geometry derived from X-ray results. This conclusion cannot necessarily be extended to *individual* studies, where a number of factors may affect the X-ray geometry. For example experimental errors, thermal-libration effects, nonbonded interactions, and crystal-packing forces are all properties of the individual molecule, its crystal structure, or of a particular structure determination. When the geometric parameters for a given substructure are averaged over a wide range of molecular environments then these non-systematic factors tend to be smoothed out. The careful choice of contributors to a given mean is of some importance, especially in terms of their individual precision, and of the structural diversity of the sample. Thus the mean geometry for a fragment which is derived from a sample of overcrowded molecules will reflect the steric factors involved, and be significantly different from a mean based on a more diverse population. The results of Fig. 5 indicate that, with careful derivation, the mean geometries of chemical fragments may be validly interpreted in terms of electronic effects.

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Table 7. *Geometric parameters* (*Fig.* 1, *Table* 3) *for the isomeric series MCDPCB, MXCPBU and NEWCPD* (*Gassman et al.*, 1983)

Distances are in Å, angles in deg.

Compound	R		d_{13}	φ	ρ	d^a_{calc}	$\lvert\tau_{15}\rvert$	$\lvert\tau_{26}\rvert$
NEWCPD	0·040	7	1·455	113·4	141·8	1·457	17, 37	2, 9
MXCPBU	0·050	6	1·498	121·2	139·5	1·478	56, 60	174, 43
MCDPCB	0·045	3	1·558	127·2	131·0	1·504	69, 85	45, 70

Note: (*a*) Calculated from the double-regression equation [equation (2)].

APPENDIX

A referee has drawn attention to a very recent paper (Gassman, Greenlee, Dixon, Richtsmeier & Gougoutas, 1983) which contains fully refined results for MCDPCB and MXCPBU, together with accurate data for the 2,4-*exo,exo* isomer of these two compounds (see Fig. 2). The most important parameters (Fig. 1) for these three structures are collected in Table 7 for completeness; the *exo,exo* isomer is designated as NEWCPD.

The most significant difference between the refined and preliminary results for MCDPCB, MXCPBU is a contraction of the intra-ring bond lengths, by ~0·02 Å in both cases (compare Tables 3 and 7). The most interesting results, however, are for NEWCPD. Here both *exo* carbonyls are in the conjugatively favourable bisected position (τ_{26} in Table 7), while the 1,3-diphenyl groups are unfavourably disposed at $|\tau_{15}|$ values very far from 90°. This results in ring geometry which is almost identical to that of ZEHREJ (Table 3), *i.e.* d_{13} is shortened, φ is low, and ρ is enlarged with respect to parent BCB (MW). NEWCPD is fitted almost exactly by the double regression [equation (2) above], with a discrepancy between observed and calculated d_{13} of only 0·002 Å. A similar comparison of d_{13} values for MXCPBU, MCDPCB (Table 7) shows increasingly large disparities (0·020, 0·054 Å) between observed and calculated parameters. However, in these structures the 1,3-diphenyl groups are approaching favourable conjugative conformations, especially in MCDPCB. None of the structures used to obtain the double-regression equation (2) were substituted in this way. Indeed, PHCPOA was rejected as a regression contributor for this very reason, and on the grounds of $t = 1$ constraints. The refined results for MCDPCB, MXCPBU show that the latter argument is only partially true, since here $t = 0$ and the inter-ring angle φ is free to expand, but only within limits set by nonbonded repulsions between all ring substituents. The situation here is complicated by the fact that MXCPBU also has one bisecting carbonyl group. Nevertheless, there is now some evidence to suggest that conjugative interactions through the 1,3 bond produce increases in d_{13} which are not fully reflected by increases in φ. Further experimental data are required before these points can be resolved.

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Parameter Refinement for Tetrafluoroterephthalonitrile at 98 K: Making the Best of a Bad Job

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Abstract

The effect of selectively excluding weak reflections from least-squares refinements of crystal structures has been examined. A systematic bias in the intensities of weak reflections may be introduced by improper treatment of prescan measurements. Omission of reflections with weak or negative measured intensity from high-order ($\sin\theta/\lambda > 0{\cdot}85$ Å^{-1}) refinements has practically no effect on the positional or vibrational parameters provided that this bias is eliminated. However, substantial errors in the parameters may be introduced by refining with only low-order reflections or even with full data sets that include low-order reflections. These conclusions are based on calculations made with a reasonably accurate and extensive data set measured for tetrafluoroterephthalonitrile ($C_8F_4N_2$) at 98 K, including all 2378 reflections accessible out to $\sin\theta/\lambda = 1{\cdot}15$ Å^{-1}.

Introduction

Van Rij & Britton (1981) determined the crystal structure of tetrafluoroterephthalonitrile at room temperature and pointed out the suitability of this compound for a low-temperature charge-density study: the molecule contains no hydrogen, all its atoms have approximately the same scattering power for X-rays, and the molecular site symmetry in the crystal is $2/m(C_{2h})$. We decided to take up the problem where van Rij & Britton had left it. Preliminary results of our low-temperature study were reported at Ottawa (Dunitz, Schweizer & Seiler, 1981). The most remarkable feature of the deformation maps we obtained is the weakness of the bonding density in the carbon–fluorine bond relative to that in the other bonds and to the lone-pair density at the nitrogen atom. Some details of the work have been described by Dunitz, Schweizer & Seiler (1982, hereinafter DSS)

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