Table 6. *Hydrogen-bond distances* (Å)

Symmetry code

(i)	$-1+x, y, z$	(iii)	$x, y-1, z$
(ii)	$1-x, y-\frac{1}{2}, -z$	(iv)	$1-x, y+\frac{1}{2}, 1-z$

N–Cl(2)^{i}	3·164 (8)	O_{aq}–Cl(2)^{i}	3·201 (8)
N–Cl(2)^{ii}	3·296 (7)	O_{aq}–Cl(2)^{iv}	3·220 (6)
N–$O_{aq}{}^{iii}$	2·795 (10)		

picrate salt (Thewalt & Bugg, 1970) and as a creatinine salt (Karle, Dragonette & Brenner, 1965). In the former, 5-HT has a *gauche* conformation and in the latter the side chain is fully extended. The structural and conformational requirements for (*R*)-alaproclate to compete with 5-HT in the uptake mechanism as well as stereochemical and electronic properties of a receptor model are discussed elsewhere (Lindberg, Thorberg, Bengtsson, Renyi, Ross & Ögren, 1978; Lindberg, Ross, Thorberg, Ögren, Malmros & Wägner, 1978).

The proposed mechanism for the 5-HT uptake requires that the distances between the protonated N and the centre of the benzene ring in (*R*)-alaproclate and 5-HT, respectively, are approximately equal. The distances obtained from the crystal structure determinations are 6·64 Å in (*R*)-alaproclate, 6·40 Å in the creatinine salt and 5·11 Å in the picrate salt of 5-HT. The distance obtained in (*R*)-alaproclate may well be compared to the corresponding distances of 6·55 and 6·11 Å in another antidepressant, the tricyclic compound chlorimipramine hydrochloride (Post & Horn, 1977).

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Acta Cryst. (1980). B**36**, 81–96

The Geometry of Small Rings. I. Substituent-Induced Bond-Length Asymmetry in Cyclopropane

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Abstract

A subfile of numeric structural data for 299 X-ray studies of cyclopropane derivatives has been retrieved from the Cambridge Crystallographic Database. The geometries of 91 rings ($R \leq 0.10$) having electron-acceptor or electron-donor substituents have been analysed. Although individual bond-length asymmetries are quantitatively small there are consistent trends to support the results of MO calculations. For π-acceptor substituents the distal ring bond is *shortened* and vicinal bonds lengthened. Mean distal-bond shortenings, relative to the individual mean C–C(ring) distance, are established for C=O, C=C and C≡N as −0·026 (5), −0·022 (4) and −0·017 (2) Å. N=C, N=N and C=N are also implicated in effective acceptor interactions. *cis*- and *trans*-bisected conformations predominate, but for C=O, and possibly

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C=C, orbital overlap appears to be effective for a range of ±30° about these ideal positions. Data for electron-donor substituents are sparse, but results for *gem*-difluoro and *gem*-dichloro substitution indicate significant distal-bond *lengthening* [+0·060 (15) for F_2, +0·025 (7) Å for Cl_2] in accord with theoretical predictions; the effect for Br is minimal. The effect of phenyl substituents is complex: they appear to accept electron density from the cyclopropane 3*e'* orbitals in the bisected conformation, but to donate electron density to the 4*e'* orbitals in the (predominant) perpendicular conformation; a mean distal-bond shortening of −0·018 (2) Å is obtained. The proposed additivity of bond-length asymmetries is found to be applicable for pure acceptor substitution and for the Cl-donor effect; data for other donors, and for donor–acceptor mixtures, are too sparse for a valid test. The mean C–C (ring) length for cyclopropane is 1·509 (2) Å over 115 occurrences.

Introduction

Cyclopropane is a prime example of a simple chemical system exhibiting high strain energy. Its physical and chemical properties and reactivity patterns are atypical of cycloalkanes and have been recognized as being analogous to those of a C=C double bond (Charton, 1970). The ability of cyclopropane to conjugate with adjacent π-acceptor groups, *e.g.* carbonyl, cyano *etc.* (Hoffmann, 1970; Hoffmann & Stohrer, 1971), and its highly effective stabilization of carbonium ions (Deno, Richey, Liu, Lincoln & Turner, 1965; Schleyer & Buss, 1969), are of particular interest to chemists. For these reasons cyclopropane and its derivatives have been the subject of considerable theoretical, structural and synthetic study over the past thirty years.

Early studies on the nature of bonding in cyclopropane (Walsh, 1947, 1949; Sugden, 1947; Coulson & Moffitt, 1947, 1949) predicted a D_{3h}-symmetric molecule having a bond length somewhat shorter than a normal C(sp^3)–C(sp^3) distance. This was confirmed by IR spectroscopy (1·524 ± 0·014 Å; Gunthard, Lord & McCubbin, 1956) and, with greater precision, by electron diffraction ($1{\cdot}509_6 \pm 0{\cdot}001_5$; Bastiansen, Fritsch & Hedberg, 1964) and by Raman spectroscopy (1·514 ± 0·002 Å; Jones & Stoicheff, 1964; Butcher & Jones, 1973).

Gas-phase studies on cyclopropyl derivatives (see Penn & Boggs, 1972, and references therein) and X-ray work on cyclopropanecarbohydrazide (Chesnut & Marsh, 1958), 2,5-dimethyl-7,7-dicyanonorcaradiene (Fritchie, 1966) and, particularly, cyclopropane-1,1-dicarboxylic acid (Meester, Schenk & MacGillavry, 1971) indicated that π-acceptor substituents produced significant bond-length asymmetry in the ring. The *distal* 2–3 bond opposite the substituent was shortened and the *vicinal* 1–2, 1–3 bonds were lengthened. This asymmetry is explicable in terms of an MO model of cyclopropane bonding (Hoffmann, 1964, 1970; Hoffmann & Davidson, 1971). In cases of π-donor substitution, *e.g.* cyclopropanone (Pochan, Baldwin & Flygare, 1969), methylenecyclopropane (Laurie & Stigliani, 1970) and particularly 1,1-difluorocyclopropane (Perretta & Laurie, 1975), gas-phase results also indicated significant bond-length asymmetry, but in a direction *opposite* to that for π acceptors. This trend is not immediately explicable on Hoffmann's (1964) MO model. The picture is further complicated by Raman results obtained for cyclopropylamine (Hendrickson & Harmony, 1969; Harmony, Bostrom & Hendrickson, 1975), where the donor substituent produces asymmetry *identical* to that observed for π acceptors.

The present paper examines the experimental evidence for ring-bond asymmetry in cyclopropane produced by a variety of acceptor and donor substituents. The relevant data are assembled from the results of X-ray structural studies as stored in the Cambridge Crystallographic Database (CCD) (Kennard, Watson, Allen, Motherwell, Town & Rodgers, 1975; Allen *et al.*, 1979). These data are augmented by pertinent results obtained by other physical methods. The observed conformations and bond-length variations are related to current theoretical models of bonding in cyclopropane and its derivatives, which are summarized briefly below.

Bonding in cyclopropanes

Three related models are available to describe the bonding in free cyclopropane: the trigonally hybridized

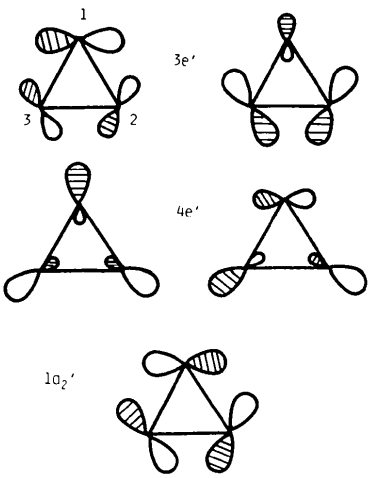

Fig. 1. Atomic-orbital representations of the two highest occupied and the unoccupied molecular orbitals of cyclopropane: (*a*) shows the 3*e'* orbitals, (*b*) the 4*e'* orbitals and (*c*) the all antibonding $1a_2'$ orbital.

model originated by Walsh (1947, 1949) and Sugden (1947), the bent-bond model of Coulson & Moffitt (1947, 1949), and the MO approach of Hoffmann (1964) based on extended Hückel-theory calculations. These basic models have been extended and modified by other workers, and variously used to explain the observed properties of cyclopropane and its derivatives. The field has been reviewed by Bernett (1967), Charton (1970) and Lathan, Radom, Hariharan, Hehre & Pople (1973).

The MO approach is the most appropriate for the present study and a full set of cyclopropane MO's is presented by Jorgensen & Salem (1973). The C–C molecular orbitals relevant to the discussion below are the two highest occupied orbitals (the $3e'$ orbitals) and the unoccupied $4e'$ and $1a_2'$ orbitals. These are depicted in Fig. 1 as atomic-orbital approximations.

Interaction with π-acceptor substituents

The MO model provides a conceptually simple explanation of the conjugative ability of cyclopropane (Hoffmann, 1970; Hoffmann & Davidson, 1971). The highest occupied orbital with the correct symmetry for interaction with π acceptors is $3e'$ (Fig. 1*a*). Maximum overlap of the cyclopropane $3e'$ orbital with low-lying unoccupied orbitals of the π system only occurs, however, when the two orbital systems are parallel (Fig. 2*a*), *i.e.* when the π-acceptor bond (R_1–R_{11}) *bisects* the ring in projection down C_1–R_1 (Fig. 2*a*; see also Fig. 4*a*,*b*). Minimum overlap occurs when the $3e'$ orbital is *perpendicular* to the relevant π orbitals (Figs. 2*b*, 4*f*).

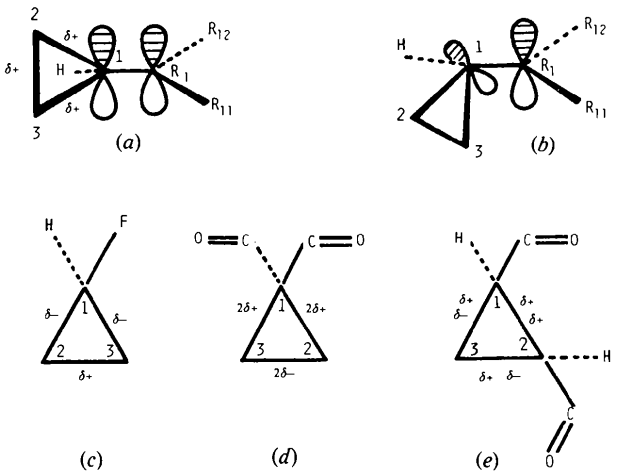

Fig. 2. Interaction of cyclopropane with electron-acceptor and electron-donor substituents. (*a*) and (*b*) illustrate the interaction between cyclopropane $3e'$ orbitals and the π orbitals of a suitable acceptor, *e.g.* R_1=R_{11} is C=O. (*a*) represents the bisected conformation (maximum overlap), together with the resultant bond-length asymmetry, where $\delta-$ = $2\delta+$. (*b*) represents the perpendicular conformation (minimum overlap). (*c*) shows the asymmetry effect of a single F substituent ($\delta+ = 2\delta-$). (*d*) shows the net asymmetry effect of 1,1-diketo substitution according to the additivity rule ($\delta- = 2\delta+$). (*e*) shows the net effect of 1,2-diketo substitution ($\delta- = 2\delta+$).

The effect of such orbital mixing is the transfer of electron density (e.d.) from cyclopropane to the π system. This will weaken the bonds for which the $3e'$ orbital has bonding character [*i.e.* the *vicinal* 1–2 and 1–3 bonds of Fig. 2(*a*)], but will strengthen the *distal* 2–3 bond, for which the $3e'$ orbital has antibonding character. *Thus the pattern of bond-length asymmetry, with respect to the average ring-bond length, is as shown in Fig.* 2(*a*) ($\delta+$ represents an increase in length, $\delta-$ a decrease; $\delta- \simeq 2\delta+$). It is this electron-density-transfer mechanism which accounts for the stability of cyclopropyl carbonium ions (Hoffmann, 1964, 1965).

Interaction with π-donor substituents

Three different orbital interactions have been invoked for the interaction between cyclopropane and a π donor, *e.g.* F, Cl *etc.* These are summarized by Jason & Ibers (1977) as: (i) σ withdrawal of e.d. from cyclopropane; (ii) donation of e.d. from a donor orbital to the $1a_2'$ (all antibonding) orbital (Fig. 1*c*); (iii) donation of e.d. to the unfilled $4e'$ orbital (Fig. 1*b*) of appropriate symmetry. Interactions (i) and (ii) serve to lengthen all bonds, while (iii) produces the bond-length asymmetry pattern predicted for π acceptors (Fig. 2*c*).

Such predictions do not agree with microwave experiments. The ring bonds in *cis,cis*-1,2,3-trifluorocyclopropane (Gillies, 1976) and in hexafluorocyclopropane (Chiang & Bernett, 1971) are uniformly 1·507 ± 0·001 and 1·505 ± 0·003 Å respectively, very close to the value for the free ring, while in cyclopropanone (Pochan, Baldwin & Flygare, 1969) the vicinal bonds are *shortened* to 1·475 ± 0·002 Å and the distal bond *lengthened* to 1·575 ± 0·002 Å; a similar pattern is shown by 1,1-difluorocyclopropane (Perretta & Laurie, 1975: vicinal = 1·464 ± 0·002, distal = 1·553 ± 0·003 Å). Interaction (iii) has, however, been invoked by Harmony, Bostrom & Hendrickson (1975) for cyclopropylamine (vicinal = 1·535 ± 0·002, distal = 1·513 ± 0·002 Å) due to the fixed symmetry of the N lone pair with respect to the molecular symmetry plane. Interaction (iii) may also be important in assessing the interaction between cyclopropane and phenyl substituents (Jason & Ibers, 1977) and is discussed below.

The conflict between theory and experiment for donor substituents has been resolved by LCAO-MO-SCF wave-function calculations for cyclopropanone and methylenecyclopropane (Deakyne, Allen & Laurie, 1977) and for a variety of fluorocyclopropanes (Deakyne, Allen & Craig, 1977; Skancke, Flood & Boggs, 1977). For these molecules a combination of interactions (i) and (ii) above *predicts the pattern of bond-length asymmetry, with respect to the average ring-bond length, shown in Fig.* 2(*c*) (here $\delta+ \simeq 2\delta-$).

The additivity principle

It has been suggested, for both π-acceptor (Hoffmann & Stohrer, 1971) and π-donor substituents (Deakyne, Allen & Craig, 1977), that *bond-length asymmetry in multiply substituted cyclopropanes should approximate a summation of the asymmetries induced by each individual substituent.* Application of this principle to 1,1- and 1,2-diketocyclopropanes is illustrated in Fig. 2(*d*),(*e*). Fig. 2(*d*) simply shows a doubling of the monosubstituent asymmetry (Fig. 1*b*). Combination of two monosubstituent asymmetries for the 1,2-compound predicts that the 1–3 and 2–3 bonds should be approximately equal and significantly shorter than the 1–2 bond between the substituted ring atoms.

Methodology

Data retrieval

In order to examine the theoretical predictions noted above, the X-ray crystallographic data for compounds containing the cyclopropane system were retrieved. A subfile of 299 DATA file entries, together with a listing of bibliographic citations, was created from the April 1979 release of CCD with the programs *CONNSER* and *RETRIEVE* (Allen *et al.*, 1979). Some statistics for the retrieved subfile are listed in Table 1. Entries with $R > 0{\cdot}10$ were omitted from the analysis unless they contained structural features of special interest. A few entries with $R \leq 0{\cdot}10$ were also rejected due to disorder, errors in coordinate lists or unusually high σ(C–C) values. This left an effective database for the analysis of 146 coordinate sets. Complete intramolecular geometry listings and a stick plot of each structure were obtained with *GEOM*78 and *PLUTO*78 (Allen *et al.*, 1979). The tables presented in the analysis were derived from special listings prepared with *GEOM*78.

Each X-ray structure referred to in this work is identified by the CCD reference code (Kennard, Watson & Town, 1972; Allen *et al.*, 1979). This consists of six alphabetic characters identifying the chemical compound and a possible two digits which trace the publication history, *e.g.* DCPEDO, CPRPCX10. A full list of references, ordered alphabetically by reference code, and giving the compound name as well as the literature citation, appears as Table 2. Reference codes are also used in the text as a conveniently brief mnemonic for individual structures. Results obtained by other physical methods are cited in the standard manner in the text and as table footnotes.

Table 1. *Statistics for cyclopropane subfile*

Number of entries retrieved	299
Number of organic entries	266
Number of entries without coordinates	81
Number of entries with coordinate errors	7
Entries with coordinates (error-free)	178
Entries with coordinates and $R \leq 0{\cdot}10$	146*
Entries with coordinates and $R \leq 0{\cdot}05$	52

* Effective database for analysis.

Generation and presentation of results

Cyclopropane–π-acceptor interactions are described in the framework of Fig. 3; for donor substituents (*e.g.* F, Cl, =O *etc.*) atom R_{11} is absent, hence D_5 and τ (see below) are also absent. The full set of parameters used in the tabulation of results is:

Code: CCD reference code.

S: number of *potential acceptor or donor* substituents at each node, *e.g.* in Fig. 3, $S = 100$ but if $R_2 = R_3 = R_5 =$ COOH then $S = 211$.

s: number of all *non*-H *substituents* at each node, *e.g.* $s = 120$ (Fig. 3) if $R_3 = R_4 = CH_3$.

R_n: chemical nature of substituent atoms, denoted by element symbol(s) and (where appropriate) an environment indicator: r = ring atom, c = chain atom, t = terminal atom; hence Ct is a methyl group.

R: crystallographic R factor (%) or physical method if not X-ray.

σ: mean σ(C–C) $\times 10^3$ Å for ring bonds.

D_n: bond lengths D_1–D_5 (Å) of Fig. 3.

Δ: mean C–C(ring) length (Å).

δ_n: D_n–Δ for the C–C(ring) bonds. A positive value indicates the lengthening (weakening) of a bond.

τ: torsion angle X_1–C_1–R_1–R_{11} (Fig. 3, and see below).

conf.: conformational descriptor (see below).

S': the number of *effective* acceptor or donor substituents at each node; the δ_n values are used, where possible, to identify the substituent interactions which contribute significantly to bond-length asymmetry.

The tables are ordered, where necessary, on increasing S,s values. In cases of multiple substitution there are several D_4, D_5, τ and conf. values; these appear as additional lines for each *code*. For π acceptor(s) at

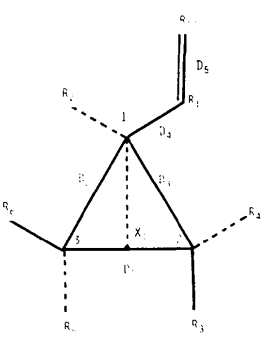

Fig. 3. Parameters and mnemonics used in the geometric analysis.

Table 2. *Bibliography*

Literature references to X-ray studies cited in the analysis are given below, ordered alphabetically by CCD reference code (see text). The compound name, author list, journal name, volume, page and year are tabulated for each entry.

ACCCYP cis-1,2-Diacetonyl-1,2,3,3-tetrachlorocyclopropane
F.P.Boer,J.J.Flynn,J.K.Hecht, J.Chem.Soc.B, 381, 1970

ACMYCR Acetylacetonato-bis(eta(2)-methylenecyclopropane) rhodium(i)
M.Green,J.A.K.Howard,R.P.Hughes,S.C.Kellett,P.Woodward
J.Chem.Soc.,Dalton, 2007, 1975

ACXBDO (5E,12E)-7beta-Acetoxybertya-5,12-diene-3,14-dione
E.N.Maslen,R.F.Toia,A.H.White,A.C.Willis
J.Chem.Soc.,Perkin 2, 1684, 1975

AIMCTY 5'-Acetyl-7,7-dichloro-2',3'-isopropylidene-3-methyl-cyclothymidine
J.Bode,H.Schenk, Cryst.Struct.Commun., 6, 645, 1977

ARITOL (-)-Aristolone
F.H.Allen,O.Kennard,J.Trotter
Acta Crystallogr.,Sect.B, 29, 1451, 1973

AXHBDO (5E,12E)-7beta-Acetoxy-15beta-hydroxybertya-5,12-diene-3,14-dione
E.N.Maslen,R.F.Toia,A.H.White,A.C.Willis
J.Chem.Soc.,Perkin 2, 1684, 1975

BARTUS10 Barbatusin p-bromobenzoyl ester benzene solvate
R.Zelnik,D.Lavie,E.C.Levy,A.H.-J.Wang,I.C.Paul
Tetrahedron, 33, 1457, 1977

BERTPP Bertyadionol photoproduct
S.R.Hall,C.L.Raston,A.H.White
Tetrahedron, 34, 753, 1978

BNPCPR 1,1-Dibromo-trans-2,3-bis(p-nitrophenyl) cyclopropane
M.E.Jason,J.A.Ibers, J.Am.Chem.Soc., 99, 6012, 1977

BPVBCP trans-1-(2'-p-Bromophenyl-vinyl)-2-benzoylcyclopropane
M.O.Dekaprilevich,L.G.Vorontsova
Zh.Strukt.Khim., 16, 426, 1975

BRTPCP 1,1-Dibromo-trans-2,3-diphenylcyclopropane
M.E.Jason,J.A.Ibers, J.Am.Chem.Soc., 99, 6012, 1977

BRVCPC 3-Phenoxybenzyl cis-3-(2',2'-dibromovinyl)-2,2-dimethylcyclopropane carboxylate
J.D.Owen, J.Chem.Soc.,Perkin 1, 1231, 1976

CEXVCP trans-1,2-bis(beta-Carboethoxyvinyl)cyclopropane
M.O.Dekaprilevich,L.G.Vorontsova
Zh.Strukt.Khim., 16, 826, 1975

CLPXCN 1,1,1a,7a-Tetrachloro-1a,2,7,7a-tetrahydro-2,7-diphenyl-2,7-epoxy-1H-cyclopropa(b)naphthalene
J.Bordner,G.R.Howard, Cryst.Struct.Commun., 4, 131, 1975

CLVCPC 3-Phenoxybenzyl cis-3-(2',2'-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate
J.D.Owen, J.Chem.Soc.,Perkin 1, 1231, 1976

CLXBHP10 exo-7-Chloro-7-phenyl-2,5-dioxabicyclo(4.1.0)heptane
J.D.Oliver,G.Henslee,P.E.Rush
Acta Crystallogr.,Sect.B, 32, 2274, 1976

CMCPYE 1-(2,2-Dichloro-3,3-dimethylcyclopropyl)ethanol
C.Romming,L.K.Sydnes
Acta Chem.Scand.Ser.B, 31, 130, 1977

CMODOD 6,6,12,12-Tetrachloro-3,3,9,9-tetramethoxy-tricyclo(9,1,0,0(5,7))dodecane
R.W.Baker,P.J.Pauling, J.Chem.Soc.,Perkin 2, 1451, 1972

CMYCZA Chloromycorrhizin A
C.Stalhandske,C.Svensson,C.Sarnstrand
Acta Crystallogr.,Sect.B, 33, 870, 1977

CPBTSX 2-Phenylcyclopropane-1-spiro-4'-(2'-benzylthio-4',5'-dihydro-6'H-1',3'-thiazine)-5'-spiro-2''-oxirane
M.L.Martinez,F.H.Cano,S.Garcia-Blanco
Acta Crystallogr.,Sect.B, 33, 3913, 1977

CPCCYP 1,1-bis-(p-Chlorophenyl)-2,2-dichlorocyclopropane
T.P.DeLacy,C.H.L.Kennard
J.Chem.Soc.,Perkin 2, 2141, 1972

CPMOIC10 1a-(p-Chlorophenoxy)1a,7b-dihydrobenzo(d)-cyclopropa(b)-pyran-3(1h)one
L.J.Guggenberger,R.A.Jacobson
Acta Crystallogr.,Sect.B, 25, 888, 1969

CPOBOC10 syn-8,8-Dichloro-4-phenyl-3,5-dioxabicyclo(5.1.0)octane
G.R.Clark,G.J.Palenik, J.Chem.Soc.,Perkin 2, 194, 1973

CPRDCA Cyclopropane-1,1-dicarboxylic acid
M.A.M.Meester,H.Schenk,C.H.MacGillavry
Acta Crystallogr.,Sect.B, 27, 630, 1971

CPRPCX10 Cyclopropanecarboxamide
R.E.Long,H.Maddox,K.N.Trueblood
Acta Crystallogr.,Sect.B, 25, 2083, 1969

CPSCPA10 (1RS,2SR)-2-((SR)-(p-Chlorophenyl)sulfinyl)-N,N,3,3-tetramethyl-cyclopropylamine
C.G.Chidester,D.J.Duchamp
Acta Crystallogr.,Sect.B, 33, 221, 1977

CPXZSH10 cis-1,5-Diphenyl-6-oxa-4-aza-spiro(2.4)hept-4-en-7-one
M.L.Martinez,F.H.Cano,S.Garcia-Blanco
Acta Crystallogr.,Sect.B, 34, 593, 1978

CTCYOC 8,8-Dichloro-tricyclo(3.2.1.0(1,5))octane
K.B.Wiberg,G.J.Burgmaier,K.-W.Shen,S.J.La Placa,
W.C.Hamilton,M.D.Newton, J.Am.Chem.Soc., 94, 7402, 1972

CYBUTB10 Cyclobutatusin p-bromobenzoyl ester
R.Zelnik,D.Lavie,E.C.Levy,A.H.-J.Wang,I.C.Paul
Tetrahedron, 33, 1457, 1977

CYCYPR cis-1,2,3-Tricyanocyclopropane
A.Hartman,F.L.Hirshfeld, Acta Crystallogr., 20, 80, 1966

CYPRCA trans-1,2-Cyclopropane dicarboxylic acid
A.L.Bednowitz, Acta Crystallogr.,Sect.A, 25, S129, 1969

CYPROT10 Cyproterone acetate
R.J.Chandross,J.Bordner
Acta Crystallogr.,Sect.B, 30, 1581, 1974

CYTCOD10 1-Cyano-tricyclo(3.3.0.0(2,8))octa-3,6-diene
G.G.Christoph,M.A.Beno, J.Am.Chem.Soc., 100, 3156, 1978

DBDPCP 1,1-Dibromo-2,2-diphenyl-cyclopropane
J.W.Lauher,J.A.Ibers, J.Am.Chem.Soc., 97, 561, 1975

DCDPCP 1,1-Dichloro-2,2-diphenyl-cyclopropane
J.W.Lauher,J.A.Ibers, J.Am.Chem.Soc., 97, 561, 1975

DCPEDO Dicyclopropyl-ethanedione
C.N.A.Lute,C.H.Stam
Rec.Trav.Chim.Pays-Bas, 95, 130, 1976

DCYBUT 1,3-Dicyanobicyclo(1.1.0)butane
P.L.Johnson,J.P.Schaefer, J.Org.Chem., 37, 2762, 1972

DMCPRC trans-2,trans-3-Dimethylcyclopropane-carboxylic acid
P.A.Luhan,A.T.McPhail, J.Chem.Soc.,Perkin 2, 2372, 1972

DTERDP Diterpene D photoproduct
S.R.Hall,C.L.Raston,A.H.White
Tetrahedron, 34, 753, 1978

EBBSHD 1-(p-Ethylbenzoyl)-benzo(6,7)spiro(2.3)hept-6-ene-4,7-dione
V.G.Andrianov,H.A.Karapetyan,Yu.T.Struchkov
Cryst.Struct.Commun., 7, 553, 1978

EBMZDC 4-Ethoxycarbonyl-5-(p-bromobenzoyloxy)-8,8-dimethyl-3,4,9,10-tetra-azatricyclo(5.3.0.0(1,6))deca-2,9-diene
R.Allmann,T.Debaerdemaeker
Cryst.Struct.Commun., 3, 205, 1974

EOCNON10 9,9-Dichloro-trans,trans-bicyclo(6.1.0)non-4-ene oxide
W.A.Szabo,M.F.Betkouski,J.A.Deyrup,M.Mathew,G.J.Palenik
J.Chem.Soc.,Perkin 2, 339, 1973

EPXHPC Methyl 2alpha,3alpha,4alpha,5alpha-diepoxy-cis-(1alphaH,2alphaH)-bicyclo(4.1.0)heptane-7alpha-carboxylate
D.J.Brauer,C.Kruger,P.J.Roberts
J.Chem.Soc.,Perkin 2, 532, 1976

EXPOCP Dimethyl 8-exo-phenylbicyclo(5.1.0)octa-2,4-diene-8-phosphonate
R.Hoge,G.Maas, Acta Crystallogr.,Sect.B, 32, 3339, 1976

EXPPCA 1-exo-Phenyl-bicyclo(2.1.0)pentane-5-carboxylic acid
G.Bernardinelli,J.-J.Combremont,R.Gerdil
Helv.Chim.Acta, 59, 1395, 1976

FMHIPR 6alpha,7alpha-Difluoromethylene-11beta-hydroxy-16alpha,17alpha-isopropylidenedioxy-21-p-bromobenzoyloxy-pregn-4-en-20-one(3,2-c)-2'-phenylpyrazole butanol solvate
E.Thom,A.T.Christensen
Acta Crystallogr.,Sect.B, 27, 573, 1971

FMPRPY 6alpha,7alpha-Difluoromethylene-16alpha-methyl-11beta,17alpha,21-trihydroxypregn-4-en-20-one(3,2-c)-2'-phenylpyrazole 21-p-bromobenzoate
A.T.Christensen
Acta Crystallogr.,Sect.B, 26, 1519, 1970

HCERGO (23R)-23-Hydroxy-3alpha,5alpha-cycloergost-7-en-6-one
M.B.Hursthouse,S.Neidle, J.Chem.Soc.,Perkin 2, 781, 1973

IPBHCZ N'-Isopropylidene-bicyclo(3.1.0)hexane-6-exo-carbohydrazide
D.G.Morris,P.Murray-Rust,J.Murray-Rust
J.Chem.Soc.,Perkin 2, 1577, 1977

Table 2 (*cont.*)

MANDAC 6beta,7beta-Methylene-17beta-hydroxy-androst-4-en-3-one 17-acetate
P.B.Braun,J.Hornstra,J.I.Leenhouts
Acta Crystallogr.,Sect.B, 26, 352, 1970

MAPCTD 12-Methyl-11,13-dioxo-12-azapentacyclo(4.4.3.0(1,6).0(2,10).0(5,7)) trideca-3,8-diene
K.J.Hwang,J.Donohue,C.Tsai
Acta Crystallogr.,Sect.B, 28, 1727, 1972

MBCPCX 1,1'-Dimethyl-bi(cyclopropyl)-2,2'-dicarboxylate
C.Jongsma,H.van der Meer
Rec.Trav.Chim.Pays-Bas, 90, 33, 1971

MBPNCP Dimethyl 2,5-dibromo-7-phenyl-norcaradiene-7-phosphonate
G.Maas,K.Fischer,M.Regitz
Acta Crystallogr.,Sect.B, 30, 2853, 1974

MCCARD 2,5-Dimethyl-7,7-dicyanonorcaradiene
C.J.Fritchie, Acta Crystallogr., 20, 27, 1966

MCMDOD 3,3-Dimethyl-4,5,9,10,11,12-hexacarboxymethyl-tetracyclo(7.2.1.0(2,4).0(2,8))dodeca-5,7,10-triene
J.P.Declercq,G.Germain,H.Henke
Cryst.Struct.Commun., 2, 405, 1973

MCPNCP Dimethyl 2,5-dichloro-7-phenyl-norcaradiene-7-phosphonate
G.Maas,K.Fischer,M.Regitz
Acta Crystallogr.,Sect.B, 30, 2853, 1974

MCPRAC 3-Methylene cyclopropane-trans-1,2-dicarboxylic acid
D.R.Petersen, Chem.Ind.(London), 904, 1956

MHHPCX Methyl 2,5-dihydroxybicyclo(4.1.0)heptane-7-carboxylate
D.J.Brauer,C.Kruger,P.J.Roberts
J.Chem.Soc.,Perkin 2, 532, 1976

MIKROL Mikrolin
H.P.Weber,T.J.Petcher, Helv.Chim.Acta, 59, 1821, 1976

MOAOSP10 3,7-Dimethyl-1,5-dioxa-3,7-diazacyclo-octane-2,4,6,8-tetraspirocyclopropane
H.Schenk, Acta Crystallogr.,Sect.B, 27, 185, 1971

MOPOPB 6-Methyl-2-oxo-1,2-diphenyl-3-oxa-2-phosphabicyclo(3.1.0)hexane
J.Jager, Z.Kristallogr., 147, 89, 1978

MOXSOC Dimethyl 6',7'-dimethyl-3'-oxospiro(oxirane-2,4'-tricyclo(3.3.0.0(2,8))oct-6-ene)-1',8'-dicarboxylate
O.Lindgren, Acta Crystallogr.,Sect.B, 34, 2638, 1978

MPBTCD10 7,8-(5-Methoxybenzo)tricyclo(4.3.1.0(2,9))deca-4,7-diene-9-phosphonic acid dimethyl ester
G.Maas,M.Regitz, Chem.Ber., 111, 1733, 1978

MPDECO (+)-6,7-Dimethyl-4-isopropyl-tricyclo(4.4.0.0(2,4))dec-1-ene-9-one
A.R.Overbeek,G.J.Olthof,N.van der Putten,H.Schenk
Cryst.Struct.Commun., 7, 679, 1978

MTCBPR meso-2,2,2',2'-Tetrachloro-3,3,3',3'-tetramethylbicyclopropyl
C.Romming,L.K.Sydnes
Acta Chem.Scand.Ser.B, 30, 963, 1976

MTPHEX endo-6-Methoxy-1,3,6-triphenyl-bicyclo(3.1.0)hex-3-ene-2-one
W.J.Seifert,T.Debaerdemaeker,U.Muller
Acta Crystallogr.,Sect.B, 31, 537, 1975

MXPCAR 7-Dimethoxyphosphoryl-7-phenyl-norcaradiene
G.Maas,K.Fischer,M.Regitz
Acta Crystallogr.,Sect.B, 30, 1140, 1974

NCUBEB10 Norcubebanone
W.E.Thiessen, Acta Crystallogr.,Sect.B, 33, 3838, 1977

NPCPMK E-2-p-Nitrophenyl-cyclopropyl methyl ketone
J.Bordner,L.A.Jones,R.L.Johnson
Cryst.Struct.Commun., 1, 389, 1972

OCTRCB Hexacyclo (9.3.2.2(4,7).0(2,9).0(3,8).0(10,12)) octadeca-13,15,17-triene-5,6-carbonate
J.J.Stezowski, Cryst.Struct.Commun., 4, 329, 1975

PBBSHD 1-(p-Propylbenzoyl)-benzo(6,7)spiro(2.3)hept-6-ene-4,7-dione
V.G.Andrianov,H.A.Karapetyan,Yu.T.Struchkov
Cryst.Struct.Commun., 7, 559, 1978

PBOPOS Dimethyl 8-phenyl-bicyclo(5.1.0)octa-2,4-diene-8-phosphonate
G.Maas, Cryst.Struct.Commun., 5, 107, 1976

PBTCOU 6-Phenyl-4-oxa-8,9:10,11-dibenzotricyclo(5.4.0.0(1,6))undeca-2,8,10-triene-5-one
R.J.F.M.van Arendonk,W.H.Laarhoven,P.A.J.Prick
J.R.Neth.Chem.Soc., 97, 197, 1978

PMCPRC10 R-(+)-2,2-Diphenyl-1-methyl-cyclopropanecarboxylic acid
C.C.Chiang,C.-T.Lin,A.H.-J.Wang,D.Y.Curtin,I.C.Paul
J.Am.Chem.Soc., 99, 6303, 1977

PORBET10 Phorbol
F.Brandl,M.Rohrl,K.Zechmeister,W.Hoppe
Acta Crystallogr.,Sect.B, 27, 1718, 1971

PXBVCP10 alpha-Cyano-3-phenoxybenzyl cis-3-(2,2-dibromovinyl)-2,2-dimethyl-cyclopropanecarboxylate
J.D.Owen, J.Chem.Soc.,Perkin 1, 1865, 1975

SDPPCX S-(+)-2,2-Diphenyl-cyclopropanecarboxylic acid
C.C.Chiang,C.-T.Lin,A.H.-J.Wang,D.Y.Curtin,I.C.Paul
J.Am.Chem.Soc., 99, 6303, 1977

SINDNC Spiro(indene-1,7'-norcaradiene)
W.Dreissig,P.Luger,D.Rewicki,C.Tuchscherer
Cryst.Struct.Commun., 2, 197, 1973

SPTZBN Spiro-(N(1)-phenyl-1,2,3-triazole-5-one-4,9'-bicyclo(6.1.0)nonane)
J.P.Declercq,G.Germain,M.P.Rousseaux,M.van Meerssche
Cryst.Struct.Commun., 3, 499, 1974

SRMTPX (SR)(RS)-Dimethyl 2-(p-tolylsulfinyl)-1,1-cyclopropane-dicarboxylate
F.Iwasaki,S.Mitamura,G.Tsuchihashi
Bull.Chem.Soc.Jpn., 51, 2530, 1978

SSMTPX (SS)(RR)-Dimethyl 2-(p-tolylsulfinyl)-1,1-cyclopropane-dicarboxylate
F.Iwasaki,S.Mitamura,G.Tsuchihashi
Bull.Chem.Soc.Jpn., 51, 2530, 1978

TCHRBA (+)-trans-Chrysanthemic acid p-bromoanilide
A.F.Cameron,G.Ferguson,C.Hannaway
J.Chem.Soc.,Perkin 2, 1567, 1975

TCYCPR 1,1,2,2-Tetracyanocyclopropane
Y.Wang,G.D.Stucky
Acta Crystallogr.,Sect.B, 29, 1255, 1973

TCYCPR01 1,1,2,2-Tetracyanocyclopropane
J.T.Lemley,P.M.Skarstad,R.E.Hughes
Acta Crystallogr.,Sect.B, 32, 35, 1976

TFPRBA trans-21,21-Tetrafluoroethylene-5alpha-pregn-17(20)-en-3beta,20-diol 3-p-bromobenzoate 20-acetate
A.T.Christensen, Atlas Steroids Struct., 1, 410, 1975

TOLIPO10 Tolypomycinone monohydrate
M.Brufani,L.Cellai,S.Cerrini,W.Fedeli,A.Vaciago
Mol.Pharmacol., 14, 693, 1978

TOXCNB Toxisterol C)1(3,5-dinitrobenzoate
A.J.de Kok,F.Boomsma,C.Romers
Acta Crystallogr.,Sect.B, 32, 2492, 1976

TPCLPR 2,2',3,3'-Tetraphenyl-3,3'-dichloro-bicyclopropane
C.G.Kouw,D.Hottentot,C.H.Stam
Cryst.Struct.Commun., 4, 623, 1975

TPCYPR10 Tri-isopropylidene cyclopropane
H.Dietrich, Acta Crystallogr.,Sect.B, 26, 44, 1970

TPXZSH10 trans-1,5-Diphenyl-6-oxa-4-aza-spiro(2.4)hept-4-en-7-one
M.L.Martinez,F.H.Cano,S.Garcia-Blanco
Acta Crystallogr.,Sect.B, 34, 593, 1978

XMTDIB 9-Hydroxy-1-methoxy-2-methyl-tricyclo(5.2.1.0(2,10))decane p-iodobenzoate
D.Caine,H.Deutsch,S.T.Chao,D.G.VanDerveer,J.A.Bertrand
J.Org.Chem., 43, 1114, 1978

more than one node, *e.g.* ring C(2), the τ value is X_2—C_2—R_n—R_{n1}, where $n = 3$ and/or 4.

Conformational descriptors (conf.)

For cyclopropane–π-acceptor interactions the torsion angle τ (X_1—C_1—R_1—R_{11}), where X_1 is the midpoint of the distal 2–3 bond, is used to describe conformation. τ is a measure of the deviation of the π system from the bisected position of Fig. 2(*a*), and commonly occurring conformations are systematized as Newman projections in Fig. 4. The bisected conformation occurs at $\tau = 0°$ [*cis*-bisected: *cb*, Fig. 4(*a*)] and at $\tau = 180°$ [*trans*-bisected: *tb*, Fig. 4(*b*)]. The perpendicular conformation (Fig. 2*b*) has $\tau = \pm 90°$ and is designated *p* (Fig. 4*c*).

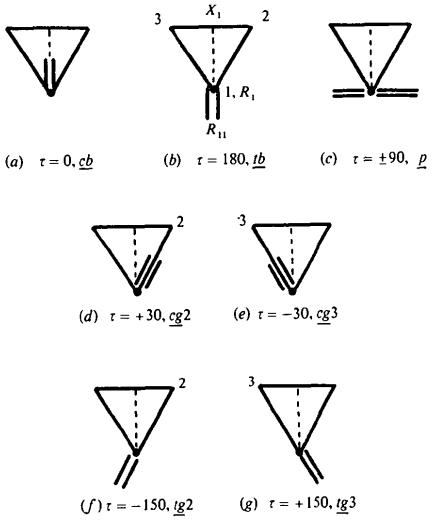

Fig. 4. Newman projections down the C_1–R_1 vector illustrating the conformation descriptors used in the analysis.

The geometrical analysis also indicates conformational projections in which the R_1–R_{11} vector is approximately parallel to one of the vicinal ring bonds. Such conformations are designated as *gauche*. The four possible arrangements (Fig. 3*d–g*) correspond to $\tau = +30°$ [*cis–gauche* (2): *cg*2], $\tau = -30°$ [*cis–gauche* (3): *cg*3], $\tau = -150°$ [*trans–gauche* (3): *tg*3], and $\tau = +150°$ [*trans–gauche* (2): *tg*2]. The differentiation between ring atoms 2 and 3 has meaning since these nodes often exhibit differing substitution patterns. Wherever possible C(2) is designated as the more highly substituted secondary site.

For phenyl substituents, where atoms R_{11} and R_{12} are part of the planar aromatic system, *cis* and *trans* have no meaning and only four conformations apply: bisected, perpendicular, *gauche* (2) and *gauche* (3). The angle τ is derived from the mean of $\tau(R_{11})$ and $\tau(R_{12})$, normalized to the range $-90 \leq \tau \leq 90°$.

Error estimates

Mean values of D_4, D_5, Δ, and δ_n are frequently quoted in this analysis. Parenthetical standard deviations are calculated for D_4, D_5 and Δ from $\sigma = [(\bar{x} - x_i)^2/m(m-1)]^{1/2}$ for m observations. For the derived δ_n values $\sigma = [(\bar{x} - x_i)^2/(m-1)]^{1/2}$ is used. Standard deviations for the torsion angle τ are not given explicitly, since τ is used solely to distinguish conformations which differ by a minimum of 30°; for the structures under discussion it is unlikely that $\sigma(\tau)$ exceeds 3°. Individual parameters determined by other physical methods (ED: electron diffraction; M: microwave; IR: infrared; N: NMR; R: Raman) are followed by error estimates in parentheses, even though these are not directly comparable to crystallographic e.s.d.'s. The physical method abbreviation replaces *R* for non-X-ray studies.

Geometry of free cyclopropane

The most accurate studies of free cyclopropane give a D_{3h}-symmetric C–C distance of 1·5096 (15) Å (ED; Bastiansen, Fritsch & Hedberg, 1964) and 1·514 (2) Å (R; Jones & Stoicheff, 1964; Butcher & Jones, 1973). Other gas-phase results on symmetrically substituted rings where, according to the additivity rule, bond-length asymmetry effects should cancel each other, are: 1·513 (9) Å (hexachloro, M; Barzdain, Fracheva & Alekseev, 1972), 1·505 (3) Å (*cis,cis*-1,2,3-trifluoro, M; Gillies, 1976) and 1·507 (1) Å (hexafluoro, ED; Chiang & Bernett, 1971).

The effective X-ray database (Table 1) contains 27 studies of derivatives having only C(sp^3) or H as substituents. The mean C–C(ring) distance at 1·508 (3) Å is in accord with the values cited above. The range of the 81 individual distances is, however, rather wide (1·469–1·535 Å), as is the range of the 27 separate means (1·490–1·530 Å). In the analysis of substituent-induced bond-length asymmetry it is therefore appropriate in deriving δ_n values to use the mean C–C length (Δ) for each individual ring, rather than the global average of the results cited here.

Interaction of cyclopropane with π-acceptor substituents

Carbonyl group

The carbonyl group is the most commonly occurring π-acceptor substituent in the cyclopropane X-ray literature. There are 20 entries (yielding 22 rings and 30 interactions) in which carbonyl is the sole π-acceptor, with only C(sp^3) or H as additional substituents. The relevant data for pure carbonyls are in Table 3, while a further 19 carbonyls appear in the mixed-substituent analyses of Tables 6 and 7.

The results of Table 3 show some consistent and significant trends:

(1) The 16 examples with $S = 100$ all show a relative shortening of the distal bond D_1; values of δ_1 range from −0·010 to −0·044 Å with 13 values in the narrow range from −0·018 to 0·033 Å. The mean overall δ_1 is −0·025 (7) Å.

(2) The predominant $S = 100$ conformation is *cb*, but *cg* and *tg* conformers are common. Only one entry, CYBUTB10, approaches the *p* conformation and it has somewhat anomalous δ_n values. The shortening of the distal bond appears to be retained for a range of ±30° about the bisected position. The mean δ_1 for the nine *cb* conformations is −0·026 (5) Å, while the mean for the

Table 3. *Analysis of cyclopropane–carbonyl conjugation*

Distances are in Å.

Code	S^a	s	R_1,R_2	R_3,R_4	R_5,R_6	R	σ	D_1	D_2	D_3	Δ	δ_1 δ_2 δ_3	D_4	D_5	τ(°)	Conf.
CPRPCX10	100	100	C=O,H	H,H	H,H	8·7	7	1·466	1·484	1·501	1·484	−18 0 +17	1·484	1·238	−7·7	*cb*
								1·449	1·493	1·488	1·477	−28 +11 +17	1·469	1·248	−4·7	*cb*
DCPEDO[b]	100	100	C=O,H	H,H	H,H	4·7	5	1·475	1·509	1·515	1·500	−23 +9 +15	1·455	1·213	−3·2	*cb*
CYPROT10[b]	100	110	C=O,H	H,C*r*	H,H	5·4	10	1·450	1·486	1·472	1·469	−19 +17 +3	1·471	1·236	−158·6	*tg2*
TOLIPO10	100	110	C=O,H	C*r*,H	H,H	5·9	6	1·485	1·502	1·542	1·510	−25 −8 +32	1·482	1·223	−24·0	*cg3*
BARTUS10	100	210	C=O,C*r*	H,C*t*	H,H	6·5	14	1·477	1·515	1·536	1·509	−32 +4 +27	1·505	1·196	−10·5	*cb*
CMYCZA[b]	100	210	C=O,C*r*	H,C*r*	H,H	3·0	5	1·484	1·521	1·529	1·511	−27 +10 +18	1·471	1·205	−2·2	*cb*
CYBUTB10	100	210	C=O,C*r*	H,C*t*	H,H	6·2	18	1·521	1·521	1·550	1·531	−10 −10 +19	1·505	1·204	−58·5	*cg3/p*
HCERGO[b]	100	210	C=O,C*r*	H,C*r*	H,H	8·4	13	1·482	1·552	1·545	1·526	−44 +26 +19	1·462	1·220	18·8	*cb/cg3*
MIKROL[b]	100	210	C=O,C*r*	H,C*r*	H,H	5·5	10	1·474	1·496	1·526	1·499	−25 −3 +27	1·443	1·226	−31·3	*cg3*
DMCPRC	100	111	C=O,H	H,C*t*	H,C*t*	8·5	7	1·477	1·509	1·521	1·502	−25 +7 +19	1·456	1·246	−7·3	*cb*
EPXHPC	100	111	C=O,H	C*r*,H	C*r*,H	5·5	5	1·464	1·507	1·519	1·497	−33 +10 +22	1·480	1·213	−2·6	*cb*
IPBHCZ	100	111	C=O,H	C*r*,H	C*r*,H	5·6	3	1·473	1·513	1·518	1·501	−28 +12 +17	1·477	1·234	1·0	*cb*
MHHPCX	100	111	C=O,H	C*r*,H	C*r*,H	4·4	3	1·491	1·520	1·522	1·511	−20 +9 +11	1·473	1·199	2·6	*cb*
ARITOL[b]	100	121	C=O,H	C*t*,C*t*	C*r*,H	5·5	8	1·500	1·505	1·535	1·513	−13 −8 +22	1·439	1·226	150·3	*tg3*
NCUBEB10	100	121	C=O,H	C*r*,C*r*	C*r*,H	4·4	4	1·489	1·532	1·520	1·514	−25 +18 +6	1·468	1·215	−166·4	*tg2*
CPRDCA	200	200	C=O,C=O	H,H	H,H	4·3	3	1·467	1·530	1·539	1·512	−45 +18 +27	1·483	1·217	−170·4	*tb*
													1·485	1·218	−9·3	*cb*
							3	1·455	1·530	1·534	1·506	−51 +24 +28	1·483	1·218	−170·5	*tb*
													1·485	1·214	−9·4	*cb*
MBCPCX	200	200	C=O,C=O	H,H	H,H	4·9	—	1·473	1·526	1·541	1·513	−40 +13 +28	1·491	1·198	162·8	*tg3/tb*
													1·507	1·232	4·6	*cb*
CYPRCA	110	110	C=O,H	H,C=O	H,H	6·2	—	1·492	1·492	1·517	1·500	−8 −8 +17	1·478	1·217	−6·3	*cb*
													1·482	1·225	−0·0	*cb*
PBBSHD[a]	210	210	C=O,C=O	C=O,H	H,H	5·8	10	1·460	1·524	1·525	1·503	−43 +21 +22	1·496	1·210	−7·2	*cb*
													1·499	1·198	2·2	*cb*
													1·536	1·218	−58·6	*cg3/p*
EBBSHD[a]	210	210	C=O,C=O	C=O,H	H,H	8·2	10	1·462	1·512	1·548	1·507	−45 +5 +41	1·461	1·226	6·2	*cb*
													1·468	1·226	−4·0	*cb*
													1·533	1·203	−59·8	*cg3/p*

(*a*) All S' values are equal to S values except for the final two entries, where $S' = 200$. (*b*) Keto group is part of extended conjugated system (see text).

seven *gauche* conformations is −0·023 (10) Å; the higher r.m.s. σ(mean) in the latter case reflects the wider δ_1 spread for *gauche* conformations. It would appear, therefore, that the bisected conformation (or something very close to it) represents a true minimum in the potential well, but the τ ranges observed here indicate that the well is relatively shallow and has a broad minimum, at least for carbonyls. This is in accord with results obtained by Kosower & Ito (1962) and Goodman & Eastman (1964).

(3) The concomitant lengthening of the vicinal bond lengths D_2, D_3 is not always symmetric, even for S = 100 *cb* conformations. Although many of the discrepancies ($d = D_3 - D_2$) are at individual structural accuracy limits it is interesting to note that d ranges from 0·002–0·023 Å (mean 0·010 Å) for *cb* conformations, but the range increases for *gauche* conformations to −0·014–0·040 Å (mean |d| 0·023 Å). The three true $g(3)$ structures (TOLIPO10, MIKROL and ARITOL) have D_3, δ_3 maximized while the two $g(2)$ entries (CYPROT10 and NCUBEB10) have larger D_2, δ_2 values.

(4) The two pure S = 200 entries (CPRDCA and MBCPCX) show an enhancement of distal-bond shortening. The mean δ_1 of −0·045 (6) Å is nearly twice the value for S = 100 indicating the approximate validity of the additivity rule for 1,1-disubstitution. The predominant conformations are *cb* and *tb* and D_2/D_3 asymmetry is less pronounced.

(5) CYPRCA provides the sole example of pure carbonyl S = 110 substitution and a further test of the additivity rule applied to 1,2-disubstitution (Fig. 2*e*). With an S = 100 δ_1 of −0·026 Å and a symmetrical vicinal lengthening of $\delta_2 = \delta_3$ = +0·013 Å the rule predicts a δ sequence of −13, −13, +26. This compares favourably with an observed sequence of −8, −8, +17. The results for CYPRCA are in line with MO theory: the 3*e*′ orbital (Fig. 1*a*) has the correct symmetry for interaction with two π acceptors on vicinal C atoms so long as they both adopt conformations close to the bisected position.

(6) PBBSHD and EBBSHD have S = 210 but the effective S' = 200. In both cases the carbonyl at C(2) adopts (or is forced to adopt) a conformation midway between *cg*3 and *p*, the distance D_4 is significantly longer than all other D_4 values in Table 3, and there appears to be little or no conjugative overlap with the cyclopropane ring. This behaviour parallels that for CYBUTB10, noted at (2) above, which also has a relatively high D_4 value and the smallest δ_1 for any S = 100 entry. Inclusion of PBBSHD and EBBSHD in the S = 200 class gives a final mean δ_1 of −0·045 (4) Å for the class.

(7) The overall mean value of D_4 (omitting the three *cg*3/*p* conformations) is 1·476 (4) Å. However, the complete substituent groups fall into two main classes: (i) simple carboxyl or keto groups; (ii) systems which are further conjugated to form −C(=O)−C=C. The latter are denoted as (*b*) in Table 3 and have a mean D_4 of 1·456 (6) Å. This is significantly shorter than the corresponding value of 1·481 (3) Å for the remaining compounds. These values, together with other means

calculated in this analysis, are important in comparing the conjugative ability of cyclopropane with that of a C=C double bond. A fuller analysis of this topic is in preparation (Allen, 1979).

(8) The mean C–C(ring) distance in Table 3 is 1·504 (3) Å, where σ is computed from individual Δ discrepancies. The value is close to free cyclopropane values and no *overall* bonding effects are indicated. The mean C=O distance is 1·218 (3) Å.

There are relatively few pertinent gas-phase results. The ED studies of cyclopropyl methyl ketone and cyclopropylcarboxyl chloride (Bartell, Guillory & Parks, 1965) give mean C–C distances of 1·510 (2) and 1·506 (3) Å respectively, but do not differentiate between distal and vicinal bonds. More recent M studies of *cis*- and *trans*-cyclopropanecarbaldehyde (Voltrauer & Schwendemann, 1971) and of cyclopropylcarboxyl chloride (Nair & Boggs, 1976) indicate distal bonds of 1·490 (2), 1·497 (3) and 1·489 (3) Å, significantly shorter than the free ring value. An IR/R study of cyclopropanecarboxylic acid has vicinal bonds of 1·53 (2) Å and a distal bond of 1·46 (2) Å (Maillols, Tabacik & Sportouch, 1976); although of limited accuracy, these results are in accord with the X-ray values. The IR/R study also reports D_4, D_5 as 1·48 (2) and 1·22 (2) Å.

Vinyl group

The generic term vinyl is used here to describe Δ–C=C derivatives. While such compounds are relatively common, only nine entries have vinyl groups, C(sp^3) and H as sole substituents. The relevant data for pure vinyls are in Table 4.

Seven of the 11 interactions adopt the *cb* or *tb* conformations and appear to be the only clear cases of conjugative overlap, exhibiting consistent distal-bond shortening. In *gauche* conformations this effect is minimized, or even reversed, in contrast to the carbonyl situation. The clearer preference for bisected conformations is, perhaps, a reflection of the relatively weak π-acceptor ability of vinyl compared to carbonyl. The results indicate that the minimum of the potential well for cyclopropane(3e′)–vinyl orbital interactions is less broad than that for carbonyl.

The mean δ_1 for the three *tb*, S = 100 entries in Table 4 is −0·022 (4) Å, marginally less than for carbonyl. Use of this value and the additivity rule (Fig. 2*e*) predicts a δ sequence for S = 110 of −11, −11, +22. Results for CEXVCP and OCTRCB follow this pattern but are quantitatively larger. The reverse calculation on these two compounds yields a rather high δ_1 of −0·040 Å and a higher overall average of

Table 4. *Analysis of cyclopropane–C=C conjugation*

Distances are in Å.

Code	S^a	s	R_1,R_2	R_3,R_4	R_5,R_6	R	σ	D_1	D_2	D_3	Δ	δ_1 δ_2 δ_3	D_4	D_5	τ(°)	Conf.
MANDAC	100	110	C=C,H	H,C*r*	H,H	4·0	7	1·518	1·510	1·512	1·513	+5 −3 −1	1·470	1·346	−160·1	*tg*2
MPDECO	100	120	C=C,H	C*t*,C*r*	H,H	4·7	6	1·487	1·525	1·533	1·515	−28 +10 +18	1·464	1·342	−174·1	*tb*
ACXBDO	100	121	C=C,H	C*t*,C*t*	C*r*,H	4·3	7	1·487	1·505	1·528	1·507	−20 −2 +21	1·470	1·330	−174·4	*tb*
AXHBDO	100	121	C=C,H	C*t*,C*t*	C*r*,H	3·6	6	1·510	1·538	1·537	1·528	−18 +10 +9	1·482	1·332	−176·5	*tb*
BERTPP	100	121	C=C,H	C*t*,C*t*	C*r*,H	6·3	10	1·510	1·505	1·521	1·512	−2 −7 +9	1·512	1·362	117·6	*p*
DTERDP	100	121	C=C,H	C*t*,C*t*	C*r*,H	6·8	20	1·535	1·501	1·514	1·517	+18 −16 −3	1·489	1·350	160·7	*tg*3
TOXCNB	100	122	C=C,H	C*r*,C*r*	C*r*,C*t*	3·5	8	1·544	1·526	1·552	1·541	+3 −15 +11	1·467	1·348	26·7	*cg*3
CEXVCP	110	110	C=C,H	H,C=C	H,H	12·2	20	1·505	1·507	1·561	1·524	−19 −17 +35	1·462	1·323	178·5	*tb*
													1·457	1·321	174·5	*tb*
OCTRCB	110	111	C=C,H	C=C,H	C*r*,H	5·2	3	1·500	1·505	1·570	1·525	−25 −20 +45	1·458	1·325	−4·4	*cb*
													1·464	1·323	4·5	*cb*

(*a*) S' = S for all bisected (*tb*,*cb*) conformations; S' = 000 for MANDAC, BERTPP, DTERDP, TOXCNB.

Table 5. *Analysis of cyclopropane–cyano conjugation*

Distances are in Å.

Code	S^a	s	R_1,R_2	R_3,R_4	R_5,R_6	R	σ	D_1	D_2	D_3	Δ	δ_1 δ_2 δ_3	D_4	D_5	τ(°)	Conf.
DCYBUT	110	110	C≡N,H	H,C≡N	H,H	5·7	5	1·481	1·484	1·503	1·489	−8 −5 +14	1·424	1·135	160·6	*tg*3
													1·424	1·135	87·1	*p*
CYCYPR	111	111	C≡N,H	C≡N,H	C=N,H	2·3	3	1·518	1·518	1·518	1·518	0 0 0	1·449	1·144	−27·2	*cg*3
TCYCPR	220	220	C≡N,C≡N	C≡N,C≡N	H,H	3·8	4	1·501	1·506	1·561	1·523	−22 −17 +38	1·449	1·137	8·7	*cb*
													1·451	1·134	142·2	*tg*3
													1·445	1·141	2·2	*cb*
													1·450	1·139	−20·6	*cg*3
TCYCPR01	220	220	C≡N,C≡N	C≡N,C≡N	H,H	5·5	2	1·515	1·512	1·558	1·529	−14 −17 +30	1·442	1·150	15·2	*cg*2/*cb*
							b	1·517	1·563	1·533	1·533	−14 −16 +30	1·443	1·147	5·2	*cb*
													1·445	1·149	−36·6	*cg*3
													1·447	1·149	156·3	*tg*3
Cyanocyclopropane[c]	100	100	C≡N,H	H,H	H,H	M	3	1·500	1·528	1·528	1·519	−19 +9 +9	—	—	—	—

(*a*) S' = S for all entries. (*b*) D_1–D_3 corrected for thermal libration effects. (*c*) Pearson, Choplin & Laurie (1975).

−0·029 (10) Å. Further quantitative evidence for distal-bond shortening by vinyl is contained in the mixed-substituent analysis of Table 6 and is presented below.

Mean values of D_4 are 1·465 (3) Å for *tb*, *cb* conformations and 1·484 (10) Å for *g*, *p* conformations. The mean Δ is somewhat high at 1·520 (4) Å, while the mean C=C is 1·336 (4) Å. The only gas-phase study (M) is of vinylcyclopropane (DeMeijere & Luttke, 1969) where values of Δ, D_4, D_5 are 1·522 (1), 1·475 (3) and 1·334 (2) Å respectively.

Cyano group

Only four pure cyanocyclopropanes have been studied by X-ray methods, but these entries (Table 5) yield 11 separate interactions, which show a wide variety of conformations. This is to be expected, since, for the formally triply bonded CN group, the $\pm p$ conformations should also be favourable.

The substitution patterns of Table 5 require application of the additivity principle to obtain δ(CN). The δ_1 values obtained for DCYBUT, TCYCPR and TCYCPR01 are −0·015, −0·019, and −0·014 Å respectively; these compare very favourably with the microwave study of cyanocyclopropane (Pearson, Choplin & Laurie, 1975) where δ_1 is −0·019 Å. The mean δ_1(CN) is therefore −0·017 (2) Å. The distal-bond length in 1,1-dicyanocyclopropane has also been measured (M; Pearson, Choplin, Laurie & Schwartz, 1975) at 1·485 Å, a value consistent with other results.

The substitutionally and crystallographically symmetric CYCYPR contains three mutually opposing CN groups and the Δ value [1·518 (3) Å] is close to free-ring values. The mean Δ over all rings in Table 5 is 1·515 (3) Å, while mean D_4 and D_5 are 1·443 (3) and 1·142 (3) Å respectively.

It appears that early reports of cyclopropane–cyano conjugation based on UV spectra (Rogers, 1947; Mohrbacher & Cromwell, 1957) are entirely vindicated, although this conclusion was challenged by Cannon, Santilli & Shenian (1959).

Mixed substituents

The pertinent data for 16 entries having mixed π-acceptor substituents [together with C(sp^3) and H] are presented in Table 6. Data for phenyl substituents,

Table 6. *Analysis of cyclopropane–mixed* (C=O, C≡N, C=C, C=N, S=O) *conjugation*

Distances are in Å.

Code	S	s	R_1,R_2	R_3,R_4	R_5,R_6	R	σ	D_1	D_2	D_3	Δ	δ_1 δ_2 δ_3	D_4	D_5	τ(°)	Conf.	S'
BPVBCP	110	110	C=O,H	H,C=C	H,H	8·5	20	1·527	1·512	1·569	1·536	−9 −24 +33	1·527	1·209	7·8	*cb*	110
													1·467	1·380	−172·6	*tb*	
AIMCTY	110	112	C=O,H	C=N,H	C*t*,C*t*	4·8	8	1·511	1·517	1·496	1·508	+3 +9 −12	1·474	1·237	−146·7	*tg*2	—
													1·474	1·371	35·5	*cg*2	
BRVCPC	110	112	C=O,H	C=C,H	C*t*,C*t*	4·4	20	1·495	1·488	1·532	1·505	−10 −17 +27	1·474	1·172	7·3	*cb*	110
													1·496	1·296	175·3	*tb*	
CLVCPC	110	112	C=O,H	C=C,H	C*t*,C*t*	6·9	22	1·481	1·485	1·494	1·487	−6 −2 +7	1·497	1·167	0·7	*cb*	110
													1·474	1·349	176·9	*tb*	
PXBVCP10	110	112	C=O,H	C=C,H	C*t*,C*t*	7·0	40	1·493	1·457	1·508	1·486	+7 −29 +22	1·449	1·225	4·1	*cb*	110
													1·413	1·317	−126·3	*tg*2/*p*	
MAPCTD	111	211	C=O,C*c*	C=C,H	C=C,H	4·6	8	1·505	1·510	1·515	1·510	−5 0 +5	1·462	1·223	−1·1	*cb*	111
													1·469	1·298	30·6	*cg*2	
													1·491	1·298	−30·4	*cg*3	
SRMTPX	210	210	C=O,C=O	S=O,H	H,H	6·3	9	1·462	1·503	1·491	1·485	−23 +18 +6	1·506	1·193	−12·2	*cb*	100
													1·505	1·193	−86·3	*p*	
													1·805	1·462	−19·5	*cg*3	
SSMTPX	210	210	C=O,C=O	S=O,H	H,H	5·0	6	1·475	1·511	1·511	1·499	−24 +12 +12	1·475	1·197	149·7	*tg*3	100
													1·514	1·189	−52·2	*cg*3/*p*	
													1·766	1·485	−122·5	*tg*2/*p*	
SPTZBN	200	211	C=O,N=N	C*r*,H	C*r*,H	6·2	5	1·470	1·532	1·529	1·510	−40 +22 +19	1·474	1·203	2·6	*cb*	200
													1·422	1·254	176·9	*tb*	
MOXSOC	210	221	C=O,C=C	C=O,C*r*	C*r*,H	3·6	4	1·511	1·521	1·518	1·517	−6 +4 +1	1·503	1·205	−156·1	*tg*2	—
													1·503	1·334	−23·1	*cg*3	
													1·478	1·201	7·8	*cb*	
MCMDOD	210	222	C=O,C=C	C*r*,C=C	C*t*,C*t*	6·2	8	1·507	1·559	1·549	1·538	−31 +21 +11	1·497	1·206	8·7	*cb*	100
													1·486	1·356	37·7	*cg*2	
													1·496	1·336	−21·1	*cg*3	
CYTCOD10	111	211	C≡N,C*r*	C=C,H	C=C,H	5·6	3	1·569	1·504	1·501	1·525	+45 −21 −24	1·438	1·143	−158·4	*tg*2	—
													1·472	1·317	22·8	*cg*2	
													1·467	1·323	−22·1	*cg*3	
MCCARD	211	211	C≡N,C≡N	C=C,H	C=C,H	3·9	3	1·500	1·554	1·558	1·537	−37 +17 +21	1·436	1·153	−65·9	*cg*3/*p*	200
													1·436	1·148	57·4	*cg*2/*p*	
													1·485	1·348	32·7	*cg*2	
													1·475	1·353	−31·4	*cg*3	
TCHRBA	110	112	C=C,H	H,C=N	C*t*,C*t*	10·9	50	1·448	1·442	1·493	1·461	−13 −19 +32	1·396	1·305	−169·9	*tb*	110
													1·321	1·358	171·2	*tb*	
EBMZDC	200	211	N=N,C=N	C*r*,H	H,C*r*	9·3	20	1·510	1·548	1·527	1·528	−18 +20 −1	1·439	1·255	33·6	*cg*2	100
													1·431	1·280	6·4	*cb*	
								1·505	1·490	1·485	1·493	+12 −3 −8	1·496	1·232	32·6	*cg*2	—
													1·436	1·284	10·3	*cb*	
CPSCPA10	100	121	S=O,H	C*t*,C*t*	N*t*,H	3·7	4	1·490	1·506	1·524	1·507	−17 0 +17	1·771	1·493	−114·1	*p*	—

which always occur in conjunction with other acceptor or donor substituents, are presented separately (Tables 7 and 10). The following trends and results are obtained from Table 6:

(1) There are four C=O, C=C combinations for $S = 110$ (BPVBCP, BRVCPC, CLVCPC and PXBVCP10). From individual δ values established above ($\delta_2 = \delta_3 = -\delta_1 \times 0{\cdot}5$, *i.e.* symmetric vicinal lengthening), the additivity rule gives $\delta(110)$ of -15, -9, $+24$. Although individual observed values vary, the mean observed δ sequence is -6, -18, $+22$, in good agreement with the derived trend.

(2) MAPCTD appears to mimic CYCYPR (Table 5) in having three mutually opposing interactions, near-zero δ values, and a Δ of 1·510 (8) Å. This occurs even though the two vinyl groups are *gauche*, an unfavourable vinyl conformation from the results of Table 4.

(3) The sulphonyl derivatives, SRMTPX and SSMTPX exhibit almost perfect $S' = 100$ (C=O) behaviour. In both cases the second C=O approaches the unfavourable *p* conformation, while $p\pi$–$d\pi$ overlap with S=O appears to be minimal. The latter observation is not contradicted by results for the other S=O derivative (CPSCPA10) which has a rather indeterminate δ pattern.

(4) Results for SPTZBN clearly indicate a π-acceptor interaction with N=N in the *tb* conformation. A δ(NN) sequence of -14, $+7$, $+7$ may be derived from the additivity rule.

(5) Data for TCHRBA appear to implicate C=N (*tb*) in an $S = 110$ interaction. A C=N (*tb*) interaction also appears to determine the asymmetry in molecule (1) of EBMZDC. However, the two derived δ(C=N) sequences differ markedly and no realistic values can be given.

(6) For MCMDOD and MCCARD the vinyl groups all appear to be in unfavourable *gauche* conformations [Table 4, but see (2) above]. MCMDOD exhibits almost perfect $S' = 100$ (C=O) behaviour, while MCCARD [$S' = 200$, (CN)] gives a δ_1(CN) of $-0{\cdot}018$ Å in excellent agreement with results deduced from Table 5.

(7) Remaining entries in Table 6 exhibit indeterminate or contradictory results. The most notable is cyanosemibullvalene (CYTCOD10) where the authors conclude that intramolecular non-bonded interactions outweigh the conjugative effect in this highly bridged molecule and account for the anomalous δ sequence.

Phenyl group (φ)

The effect of phenyl substituents has been examined by Lauher & Ibers (1975) and Jason & Ibers (1977) from a limited data set containing a high proportion of phenyl,halogen mixed substituents. These acceptor–donor combinations will be discussed in a later section.

There are no examples of pure phenyl substitution in the current database. Table 7 presents results for 17 (φ, A=B) acceptor combinations; a small subset having (φ, P=O) disubstitution at C(1) are given in Table 7(*b*). In all cases the additivity rule is required to obtain $\delta(\varphi)$ sequences. The trends exhibited in Table 7 are not so clear as in other analyses, but some conclusions may be drawn:

(1) NPCPMK, SDPPCX and PMCPCR10 are the only pure φ, C=O combinations. Using δ(C=O) of -26, $+13$, $+13$ we obtain $\delta(\varphi)$ as indicated in Table 7. These values agree well and give a mean δ_1 of $-0{\cdot}018$ (2) Å. However, NPCPMK adopts the expected *b* conformation, while SDPPCX and PMCPCR10 are *p*. Since the *p* conformation offers no possibility of a π-acceptor interaction with cyclopropane $3e'$ orbitals the only explanation lies in *donation* of φ electron density into unfilled $4e'$ orbitals (see the discussion on bonding above). This mechanism is that proposed by Jason & Ibers (1977).

(2) CPBTSX shows a typical $S = 110$ δ sequence, from which δ(NC) = -18, $+9$, $+9$. Application of these values to CPXZSH10 and TPXZSH10 is complex, since a φ interaction at $\tau = -55$ or $-41°$ seems unlikely. Both $S' = 200$ and $S' = 210$ give reasonable δ_1 agreement, but $S' = 210$ gives the best overall δ_n agreement. There is, however, some evidence for a φ interaction at $\tau \simeq 50°$ in EXPPCA, which has a somewhat distorted $S' = 110$ δ sequence.

(3) The diversity of other substitution patterns in Table 7(*a*) is such that no consistent trends can be observed and no further firm conclusions drawn.

(4) The results of Table 7(*b*) fall into two distinct groups (assuming P=O as a possible interacting substituent) with $S' = 200$ and $S' = 211$. The former group yields fairly consistent δ(P=O, φ) and a δ_1 (P=O, φ) of $-0{\cdot}028$ (7) Å. Application of these results to $S' = 211$ entries, and with some vinyl overlap at $\tau \simeq \pm 30°$, would predict a δ sequence of $+4$, $+3$, $+3$; the observed mean $\delta(211)$ is $+1$, $+5$, -5. The consistency shown in Table 7(*a*) is possibly indicative of some small cyclopropane–P=O interaction with a δ_1 of *ca* $-0{\cdot}01$ Å. The *p* conformation is uniformly adopted by all φ rings in Table 7(*b*), presumably because steric interactions prohibit *b* conformers.

(5) The mean Δ for all rings in Table 7 is 1·517 (3) Å; the mean D_4 for phenyl substituents in the *b* or *p* conformations is 1·502 (3) Å. The mean C–P, P=O distances (Table 7*b*) are 1·782 (4) and 1·456 (4) Å.

Interaction of cyclopropane with electron-donating substituents

There are relatively few X-ray entries having only electron-donor substituents, together with C(sp^3) and H. Most of these are pure Cl derivatives. The relevant

Table 7. *Analysis of cyclopropane–(phenyl, A=B) and cyclopropane–(P=O, phenyl, A=B) mixed interactions*

Distances are in Å.

Code	S	s	R_1,R_2	R_3,R_4	R_5,R_6	R	σ	D_1	D_2	D_3	Δ	δ_1	δ_2	δ_3	D_4	D_5	τ(°)	Conf.	S'
(*a*) Cyclopropane–(phenyl, *A=B*)																			
NPCPMK	110	110	C=O,H	H,Ph	H,H	9·2	10	1·474	1·488	1·513	1·492	−18	−4	+21	1·469	1·234	8·6	*cb*	110
												−16	+8	+8[a]	1·501	1·379	4·3	*b*	
CPBTSX	110	120	N=C,C*r*	Ph,H	H,H	4·9	4	1·503	1·498	1·530	1·510	−7	−12	+20	1·434	1·257	158·4	*tg*3	110
															1·478	1·387	70·4	*p*	
EXPPCA	110	121	C=O,H	Ph,C*r*	C*r*,H	7·0	7	1·530	1·517	1·547	1·531	−1	−14	+16	1·480	1·206	11·8	*cb*	110
															1·472	1·380	−50·0	—	
CPXZSH10	210	210	C=O,N=C	Ph,H	H,H	4·5	7	1·471	1·500	1·547	1·506	−35	−6	+41	1·461	1·223	6·0	*cb*	210
															1·435	1·275	171·6	*tb*	or
															1·487	1·372	−55·0	—	200
TPXZSH10	210	210	C=O,N=C	H,Ph	H,H	4·5	3	1·477	1·511	1·547	1·512	−35	−1	+35	1·473	1·195	−3·3	*cb*	210
															1·426	1·268	−176·4	*tb*	or
															1·488	1·389	−40·8	—	200
SDPPCX	210	210	Ph,Ph	C=O,H	H,H	4·3	5	1·510	1·482	1·533	1·505	−5	−23	+28	1·510	1·386	86·6	*p*	210
												−18	+9	+9[a]	1·509	1·377	71·2	*p*	
															1·469	1·210	−5·5	*cb*	
PMCPRC10	210	220	Ph,Ph	C=O,C*l*	H,H	3·7	4	1·504	1·489	1·548	1·514	−10	−25	+34	1·504	1·386	72·0	*p*	210
												−19	+9	+10[a]	1·512	1·379	−85·9	*p*	
															1·484	1·204	−21·2	*cg*3	
SINDNC	211	211	C=C,Ph	C=C,H	C=C,H	5·7	5	1·520	1·533	1·535	1·529	−9	+4	+6	1·476	1·340	−177·6	*tb*	—
															1·479	1·394	−1·8	*b*	
															1·465	1·331	−25·8	*cb*3	
															1·471	1·326	28·4	*cg*2	
MTPHEX	211	212	C=O,Ph	C=C,H	Ph,O*c*	6·0	10	1·527	1·525	1·512	1·521	+6	+4	−9	1·523	1·216	−143·0	*tg*2	—
															1·478	1·381	−59·4	—	
															1·470	1·338	−27·0	*cg*3	
															1·478	1·381	48·6	—	
PBTCOU	221	221	C=O,Ph	C=C,Ph	Ph,H	3·5	5	1·499	1·540	1·552	1·530	−31	+10	+22	1·475	1·203	−156·6	*tg*2	—
															1·499	1·386	87·3	*p*	
															1·477	1·304	−23·2	*cg*3	
															1·490	1·396	−30·5	*cg*3	
															1·473	1·396	28·4	*cg*2	
(*b*) Cyclopropane–(P=O, phenyl, *A=B*)																			
MPBTCD10	200	200	P=O,Ph	C*r*,H	C*r*,H	3·0	7	1·493	1·526	1·528	1·516	−23	+10	+12	1·762	1·477	−103·3	*p*	200
															1·514	1·409	−26·0	*cg*3	
PBOPOS	200	200	P=O,Ph	C*r*,H	C*r*,H	6·3	12	1·483	1·530	1·534	1·516	−33	+14	+18	1·784	1·448	0·0	*cb*	200
															1·510	1·394	−88·7	*p*	
MOPOPB	200	200	P=O,Ph	C*r*,H	C*t*,H	4·7	6	1·486	1·523	1·511	1·507	−21	+16	+5	1·788	1·460	−97·1	*p*	200
															1·498	1·378	−73·7	*p*	
EXPOCP	210	210	P=O,Ph	C=C,H	C*r*,H	4·5	6	1·469	1·522	1·526	1·506	−37	+16	+20	1·781	1·454	−11·7	*cb*	200
															1·511	1·388	87·7	*p*	
															1·496	1·325	88·3	*p*	
MBPNCP	211	211	P=O,Ph	C=C,H	C=C,H	5·7	17	1·549	1·552	1·528	1·543	+6	+9	−15	1·782	1·442	10·6	*cb*	211
															1·511	1·390	88·1	*p*	
															1·495	1·329	−31·7	*cg*3	
															1·479	1·327	28·8	*cg*2	
MCPNCP	211	211	P=O,Ph	C=C,H	C=C,H	3·8	5	1·517	1·528	1·530	1·525	−8	+3	+5	1·791	1·458	−21·3	*cg*3	211
															1·492	1·384	89·3	*p*	
															1·450	1·320	−29·8	*cg*3	
															1·463	1·318	28·2	*cg*2	
MXPCAR	211	211	P=O,Ph	C=C,H	C=C,H	4·1	4	1·535	1·533	1·525	1·531	+4	+2	−6	1·785	1·456	10·0	*cb*	211
															1·494	1·392	−88·6	*p*	
															1·475	1·338	−26·7	*cg*3	
															1·468	1·340	28·1	*cg*2	

(*a*) Derived δ values for single phenyl substituent.

Table 8. *Interaction of cyclopropane with strong electron donors*

Distances are in Å.

Code	S	s	R_1,R_2	R_3,R_4	R_5,R_6	R	σ	D_1	D_2	D_3	Δ	δ_1	δ_2	δ_3	D_4[a]	D_5	τ(°)	Conf.
1,1-Difluoro-	200	200	F,F	H,H	H,H	M[b]	2	1·553	1·464	1·464	1·494	+59	−30	−30	1·355	—	—	
1,2,3-Trifluoro-	111	111	F,H	F,H	F,H	M[c]	3	1·505	1·505	1·505	1·505	0	0	0	1·354	—	—	
Hexafluoro-	222	222	F,F	F,F	F,F	M[d]	1	1·507	1·507	1·507	1·507	0	0	0	1·314			
FMPRPY	200	211	F,F	C=C,H	C*c*,H	6·5	10	1·573	1·450	1·450	1·491	+82	−41	−41	1·374	—	—	
															1·500	1·341	139·9	*tg*3
FMHIPR	200	211	F,F	C=C,H	C*c*,H	5·7	8	1·520	1·444	1·465	1·476	+44	−32	−11	1·355	—	—	
															1·490	1·317	140·7	*tg*3
TFPRBA	220	222	F,F	F,F	C=C,C*c*	7·7	—	1·516	1·458	1·456	1·477	+39	−19	−21	1·337	—	—	
															1·516	1·328	−114·4	*p*
Cyclopropanone	100	100	=O	H,H	H,H	M[e]	2	1·575	1·475	1·475	1·508	+67	−33	−33	1·191	—	—	
Methylene-	100	100	=C	H,H	H,H	M[f]	1	1·542	1·457	1·457	1·485	+57	−28	−28	1·332	—	—	
ACMYCR	100	100	=C	H,H	H,H	6·6	18	1·517	1·479	1·463	1·486	+31	−7	−23	1·404	—	—	
								1·519	1·437	1·459	1·472	+47	−35	−13	1·440	—	—	
MCPRAC	111	111	=C	C=O,H	C=O,H	17·0	—	1·545	1·490	1·491	1·509	+36	−19	−18	1·316	—	—	
															1·480	1·254	−161·1	*tg*2
															1·482	1·265	23·5	*cg*2
TPCYPR10	111	111	=C	=C	=C	9·8	4	1·442	1·463	1·447	1·451	−9	+12	−4	1·333	—	—	

(*a*) Mean D_4 values are given for multiple donor substitution. (*b*) Perretta & Laurie (1975). (*c*) Gillies (1976). (*d*) Chiang & Bernett (1971). (*e*) Pochan, Baldwin & Flygare (1969). (*f*) Laurie & Stigliani (1970).

Table 9. *Asymmetry in chlorocyclopropanes*

Distances are in Å.

Code	S	s	R_1,R_2	R_3,R_4	R_5,R_6	R	σ	D_1	D_2	D_3	Δ	δ_1 δ_2 δ_3	D_4[a]	S'
(*a*) Gas-phase results														
Monochloro-	100	100	Cl,H	H,H	H,H	M[b]	4	1·514	1·513	1·513	1·513	+1 0 0	1·740	—
1,1-Dichloro-	200	200	Cl,Cl	H,H	H,H	ED[c]	4	1·510	1·510	1·510	1·510	0 0 0	1·758	—
1,1-Dichloro-	200	200	Cl,Cl	H,H	H,H	M[d]	4	1·534	1·532	1·532	1·533	+1 −1 −1	1·734	—
1,1-Dichloro-	200	200	Cl,Cl	H,H	H,H	N[e]	—	1·544	1·480	1·480	1·501	+42 −21 −21	1·756	200
Hexachloro-	222	222	Cl,Cl	Cl,Cl	Cl,Cl	ED[f]	9	1·514	1·513	1·513	1·513	+1 0 0	1·734	222
(*b*) X-ray results														
CMODOD	200	211	Cl,Cl	*Cr*,H	*Cr*,H	4·3	5	1·546	1·496	1·495	1·512	+34 −16 −17	1·760	200
CPOBOC10	200	211	Cl,Cl	*Cr*,H	*Cr*,H	8·9	20	1·529	1·476	1·465	1·490	+39 −14 −25	1·776	200
								1·524	1·488	1·508	1·507	+17 −19 +1	1·755	200
EOCNON10	200	211	Cl,Cl	*Cr*,H	*Cr*,H	4·0	4	1·519	1·488	1·489	1·499	+20 −11 −10	1·762	200
CMCPYE	200	221	Cl,Cl	*Ct*,*Ct*	*Cr*,H	4·0	5	1·517	1·483	1·502	1·501	+16 −18 +1	1·750	200
MTCBPR	200	221	Cl,Cl	*Ct*,*Ct*	*Cr*,H	5·1	2	1·537	1·503	1·507	1·516	+21 −13 −9	1·760	200
CTCYOC	200	222	Cl,Cl	*Cr*,*Cr*	*Cr*,*Cr*	6·5	12	1·571	1·457	1·457	1·495	+76 −38 −38	1·760	200
ACCCYP	211	222	Cl,Cl	Cl,*Cr*	Cl,*Cr*	6·5	10	1·516	1·498	1·485	1·500	+16 −2 −15	1·748	211
CLPXCN	211	222	Cl,Cl	Cl,*Cr*	Cl,*Cr*	5·1	7	1·515	1·512	1·498	1·508	+7 +4 −10	1·749	211

(*a*) The mean D_4 (C–Cl) is given. The overall mean D_4 (X-ray) is 1·758 (4) Å. (*b*) Schwendemann, Jacobs & Krigas (1974). (*c*) Alekseev, Barzdain & Shostakovskii (1972). (*d*) Flygare, Narath & Gwinn (1962). (*e*) Cole & Gilson (1975). (*f*) Barzdain, Fracheva & Alekseev (1972).

gas-phase and X-ray data for known strong electron donors are collected in Table 8; data for Cl derivatives are in Table 9.

The M studies of the =O, $=CH_2$ and F_2 derivatives have δ_1 values of +0·067, +0·057 and +0·060 (F_2). The X-ray data are sparse, and not directly comparable, since π-acceptor substituents are often present. However, conjugative vinyl overlap is doubtful in the three fluorinated steroids, and asymmetry in FMPRPY and FMHIPR is in the expected direction, with a mean close to the gas-phase result. Results for TFPRBA are not as predicted by the additivity rule (δ = +30, +30, −60). Results for ACMYCR follow the correct pattern but asymmetry is less than for methylenecyclopropane due to the π interaction with Rh. Results for TPCYPR10 show a δ sequence approaching zero, as expected for three symmetric and opposing substituents, and the Δ value of 1·451 (4) Å reflects the substantial rehybridization of the ring C atoms.

The results for chlorocyclopropanes are of more interest. The early ED and M studies indicated that Cl did not produce any bond-length asymmetry (entries 3 and 5, Table 9), but significant asymmetry was detected in a NMR study (Cole & Gilson, 1975). In their study of fluorocyclopropanes, Deakyne, Allen & Craig (1977) suggest that this latter structure is more likely to be correct on theoretical grounds; this is borne out by the X-ray results. The seven dichloro derivatives all show a consistent lengthening of the distal bond. If the anomalously high result for CTCYOC is omitted, a mean $\delta_1(Cl_2)$ of +0·024 (9) Å is obtained. Since the additivity rule predicts that S = 211 entries should behave as S = 100, the results for ACCCYP and CLPXCN are in accord with the other entries. A final mean $\delta_1(Cl_2)$ of +0·025 (7) Å is obtained from all entries except CTCYOC.

Several mixed acceptor–donor substituted rings exist in the X-ray literature, but no acceptable subset exists for acceptor–donor groups except those involving phenyl group(s) and (usually) halogens. Results for this subset are collected in Table 10, in which S,S' are meaningless and are omitted. The following points may be made:

(1) DCDPCP shows a shortening of the distal bond opposite the φ_2 groups and a lengthening of the distal bond opposite Cl_2. This is to be expected since both φ groups are in the *p* conformation. The additivity rule predicts a δ sequence of −49, +4, +5, which is qualitatively correct but more than double the observed values.

(2) DBDPCP, DNPCPR and BRTCTP indicate that Br plays little or no part as a donor substituent. DBDPCP has a δ sequence that is qualitatively correct for two phenyl–cyclopropane (4*e*′) orbital interactions, having both φ groups approximately perpendicular. In BNPCPR and BRTCTP the φ groups appear to be in unfavourable conformations giving nearly symmetric rings and Δ values close to those for the free ring.

(3) In TPCLPR the φ conformations are favourable and the additivity rule would predict δ_n = +4, −16, +11, remarkably (and fortuitously?) close to experimental values for both independent molecules.

(4) Results for CPMOIC10 are qualitatively similar to those for DCDPCP and indicate distal lengthening of *ca* +0·024 Å opposite the dioxa substituents. There is further evidence for distal lengthening by oxa substituents in XMTOIB, PORBET10 and MOAOSP10.

Summary and conclusions

This work presents a review of the geometry of cyclopropane in 91 compounds having electron-accepting or

Table 10. *Analysis of cyclopropane–(phenyl,donor) mixed substitutions*

Parameters S and S' have no real significance in this analysis and are omitted. Distances are in Å.

Code	s	R_1,R_2	R_3,R_4	R_5,R_6	R	σ	D_1	D_2	D_3	Δ	δ_1	δ_2	δ_3	D_4	D_5	$\tau(°)$	Conf.
CPMOIC10	120	Ph,H	O,O	H,H	6·9	15	1·478	1·542	1·507	1·509	−31	+33	−2	1·452	1·403	−31·9	*cg*3
CPCCYP	220	Ph,Ph	Cl,Cl	H,H	6·1	10	1·484	1·473	1·472	1·476	+8	−3	−4	1·498	1·396	−78·4	*p*
														1·498	1·406	79·7	*p*
							1·546	1·517	1·543	1·535	+11	−18	+8	1·507	1·371	−85·1	*p*
														1·526	1·387	81·8	*p*
DCDPCP	220	Ph,Ph	Cl,Cl	H,H	3·4	3	1·490	1·529	1·519	1·513	−23	+16	+6	1·495	1·387	77·8	*p*
														1·505	1·389	−71·9	*p*
DBDPCP	220	Ph,Ph	Br,Br	H,H	3·5	6	1·476	1·507	1·509	1·497	−21	+10	+12	1·509	1·389	−73·2	*p*
														1·493	1·381	77·8	*p*
BNPCPR	112	Ph,H	H,Ph	Br,Br	3·5	6	1·515	1·515	1·516	1·515	0	0	+1	1·492	1·387	−51·7	—
														1·492	1·387	51·7	—
BRTCTP	112	Ph,H	H,Ph	Br,Br	2·8	5	1·515	1·515	1·518	1·516	−1	−1	+2	1·487	1·392	−48·0	—
														1·487	1·392	48·0	—
TPCLPR	211	Ph,Cl	Ph,H	△,H	5·0	6	1·523	1·506	1·519	1·516	+7	−10	+3	1·476	1·392	−16·4	*b*/*cg*3
														1·478	1·379	77·3	*p*
							1·519	1·501	1·526	1·515	+4	−14	+11	1·490	1·379	−37·4	*cg*3
														1·494	1·388	83·9	*p*
CLXBHP10	211	Ph,Cl	Or,H	Or,H	6·8	4	1·492	1·505	1·519	1·505	−13	0	+14	1·473	1·374	−87·7	*p*

Table 11. *Results of the analysis*

δ_1 values (Å)

C=O	−0·026 (5)	C≡N	−0·017 (2)
C=C	−0·022 (4)	N=N	−0·014 (–)
N=C	−0·018 (–)	Phenyl	−0·018 (2)
Cl_2	+0·025 (7)	F_2	+0·060 (–)

Mean bond lengths (Å)

Substituent	Table	$\bar{\Delta}$	$\bar{D}_4$	$\bar{D}_5$
C=O	3	1·504 (3)	1·456 (6)	1·218 (3)
			1·481 (3)	—
C=C	4	1·520 (4)	1·465 (3)	1·336 (4)
			1·484 (10)	—
C≡N	5	1·515 (3)	1·443 (3)	1·142 (4)
Mixed acceptor	6	1·508 (3)	—	—
Phenyl	7	1·517 (3)	1·502 (3)	1·387 (4)
Cl donor	9	1·503 (3)	1·759 (4)	—
Mixed donor	10	1·509 (4)	—	—
Overall[a]		1·510 (2) for 88 rings		

(*a*) Inclusion of 27 unsubstituted rings (see text) gives $\bar{\Delta}$ = 1·5095 (17) Å.

-donating substituents attached to the ring. A further 27 compounds having only C(sp^3) or H substituents were used to establish a mean C—C(ring) distance. A further 28 compounds with $R \leq 0{\cdot}100$ were omitted because they have unique substitution patterns or because the ring forms part of a highly bridged system, so that steric interactions dominate their geometry. Observed substituent-induced bond-length asymmetry has been examined in the light of current theoretical treatments of ring-substituent orbital overlap. Although individual bond-length asymmetries are often quantitatively small, there are self-consistent and statistically significant trends to support the following conclusions:

(1) There is ample evidence that electron density is transferred from cyclopropane 3*e*′ orbitals to low-lying π orbitals of C=O, C=C and C≡N. This shortens the distal ring bond and lengthens the vicinal bonds. Mean values for the distal-bond shortening (δ_1), relative to the mean C—C ring distance (Δ) are in Table 11, together with other relevant averages. The bisected conformation dominates C=O, C=C interactions and yields symmetric vicinal lengthening of one half the absolute value of δ_1. The C=O interaction is best characterized and shows a broad minimum in the potential well corresponding to τ ranges of ±30° about the *cb* and *tb* positions. Pronounced asymmetry of vicinal bonds is observed as the τ limits are approached. There is some evidence to suggest that the minimum of the C=C potential well is less broad.

(2) There is some evidence for a similar acceptor mechanism for N=N, N=C and C=N substituents although no δ_1 value was obtained for the latter.

(3) The relative acceptor effectiveness is in the order C=O > C=C > N=C ≃ C≡N > N=N.

(4) Phenyl substituents appear to cause distal-bond shortening in both *b* and *p* conformations and have δ_1 approximately equivalent to that for C≡N. The *p* conformation dominates, presumably due to steric interactions, and *donation* of electron density from phenyl to cyclopropane 4*e*′ orbitals is presumed to account for the effectiveness of this conformation.

(5) Electron-donor substituents having orbitals of the necessary symmetry to interact with the cyclopropane $1a_2'$ orbital cause distal-bond lengthening and vicinal shortening, in contradiction to the simple MO model. The observed geometries agree well with more recent theoretical models for donor substituents (Deakyne *et al.*, 1977).

(6) The effectiveness of Cl as an electron donor is established and a δ_1 value of +0·026 (7) Å obtained for *gem*-dichloro substituents.

(7) The additivity rule for bond-length asymmetries (δ) has been applied with some success to acceptor and

donor interactions. Data on mixed acceptor–donor compounds are too sparse for a valid test on these interactions.

(8) There is a need for more accurate structural data for donor substituents and for the less-common π acceptors.

(9) The average Δ and D_4 established in this analysis, especially for π acceptors, should provide a means of comparing the cyclopropane ring with the C=C double bond, which it resembles in many of its properties. Such an analysis is in preparation (Allen, 1979) and further work on other small rings is in progress.

(10) The mean C–C(ring) distance ($\bar{\Delta}$) over 88 rings having acceptor or donor substituents and studied by X-ray methods is 1·510 (2) Å, where the σ value is obtained from individual Δ discrepancies. This is close to the value of 1·508 (3) Å from 27 rings having only C(sp^3) or H substituents. There is no evidence that either acceptor or donor substitution causes systematic changes in Δ. The mean Δ over all 115 X-ray determinations of $1{\cdot}509_5$ (1_7) should be compared with the electron-diffraction value cited in the *Introduction*.

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Empilement Cristallin et Séparation Spontanée des Enantiomères. Structure Cristalline de la *N*-(Phényl-1 éthyl)-isobutyramide

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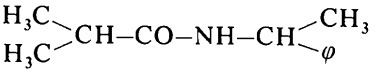
Abstract

The structure of racemic *N*-(1-phenylethyl)isobutyramide ($C_{12}H_{17}NO$, $M_r = 191$) has been determined from three-dimensional X-ray diffractometer data. The compound crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 10{\cdot}966$ (3), $b = 9{\cdot}653$ (3), $c = 11{\cdot}277$ (4) Å, $\beta = 98{\cdot}57$ (4)°, $d_x = 1{\cdot}06$ Mg m^{-3}, $Z = 4$. The structure was solved by *MULTAN* and refined by least-squares methods to $R = 0{\cdot}051$ with 1461 reflections. Homochiral molecules are hydrogen bonded and heterochiral molecules experience only van der Waals forces.

Introduction

Lors d'une étude précédente (Aubry, Protas, Cung & Marraud, 1980) nous avons décrit la structure cristalline de la *N*-(phényl-1 éthyl)-acétamide qui subit, lors de la cristallisation, une séparation spontanée des énantiomères. Afin de mettre en évidence l'influence du volume des extrémités de chaîne sur ce comportement, nous avons examiné la structure à l'état solide de la *N*-(phényl-1 éthyl)-isobutyramide sur un monocristal obtenu à partir d'une solution du racémique.



La numérotation atomique est portée sur la Fig. 1.

Les cristaux ont été obtenus par lente évaporation d'une solution racémique dans l'acétate d'éthyle. Une fine aiguille de longueur inférieure à 0,3 mm a été utilisée pour enregistrer le réseau réciproque. Les intensités diffractées ont été enregistrées sur un diffractomètre automatique CAD-4F Nonius, muni d'un monochromateur au graphite, en utilisant le rayonnement $K\alpha$ du cuivre. Sur les 2241 réflexions enregistrées dans le domaine de Bragg compris entre 1 et 70°, 1461 réflexions indépendantes, satisfaisant au critère statistique $I > 3\sigma(I)$ ont été conservées pour résoudre la structure. Le mode de balayage $\omega - 5\theta/3$ a été utilisé. Chaque réflexion a été corrigée des phénomènes de Lorentz et de polarisation. L'absorption a été négligée ($\mu R = 0{,}14$).

La structure a été déterminée à l'aide de la chaîne de programmes *MULTAN* (Germain, Main & Woolfson, 1970). L'affinement des paramètres atomiques, sans schéma de pondération et tenant compte des corrections d'extinction secondaire isotrope ($g = 0{,}0165$), par une méthode de moindres carrés avec matrice complète

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