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THE GEOMETRY OF SMALL RINGS—IV

MOLECULAR GEOMETRY OF CYCLOPROPENE AND ITS DERIVATIVES[†]

FRANK H. ALLEN

Crystallographic Data Centre University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

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Abstract—Numeric structural data for 34 derivatives of cyclopropene and cyclopropenium ion have been retrieved from the Cambridge Crystallographic Database and analysed in conjunction with available gas-phase results. Geometric data indicate that the vinylic C atoms in cyclopropene use $\sim sp^{1.19}$ hybrids in bond formation to substituents and contribute $\sim sp^{2.68}$ hybrids to the ring σ-framework. The D_{3h}-symmetric cyclopropenium ion has a bond length of 1.373(3)Å, which can be related to distances in unstrained systems. Comparison of data for cyclopropenylidenes and 3,3-difluorocyclopropene with analogous cyclopropanes shows that π-donor effects (distal bond lengthening, vicinal bond shortening) are apparent in cyclopropene. Rehybridization and π-donation are largely responsible for cyclopropenylidene geometry, rather than significant contributions from dipolar and pseudo-aromatic resonance forms. Insufficient data exist to quantify the effect of π-acceptor substituents on cyclopropene, but some lengthening of vicinal bonds is apparent. Three major bonding patterns are exhibited by organometal derivatives of cyclopropenium and cyclopropene.

Cyclopropene **1** was first prepared some sixty years ago[1] but, despite its unusual structure exhibiting high Baeyer strain, the molecule received minimal attention until the late 1950's. Two factors led to a resurgence of interest: firstly developments in carbene chemistry led to new and convenient syntheses of cyclopropene derivatives,[2] secondly it was realized[3] that the cyclopropenyl cation **3** obeyed the Hückel $(4n+2)\pi$-rule with $n=0$. This predicted aromatic stability of cyclopropenium ion was confirmed by synthesis[4,5] of the first stable salt: 1,2,3-triphenyl-cyclopropenium cyanide. Since that time chemical and theoretical interest has been considerable and reviews have appeared on cyclopropene **1**,[2] cyclopropenyl cation **3**,[6] methylenecyclopropenes (triafulvenes, **4**),[7] cyclopropenones **5a**[8] and benzocyclopropenes.[9] The extent of theoretical interest is indicated by the extensive lists of references cited by Halton.[10]

Previous papers in this series[11–13] have examined the solid-state geometry of the saturated analogue cyclopropane **2** in some detail. In Part I[11] an attempt was made to quantify ring-bond length asymmetry induced by π-acceptor and π-donor substituents. For π-acceptors (–C=O, –C=C, –C≡N etc.) at C(3) in **2** the distal (1–2) bond is shortened and the vicinal (1–3, 2–3) bonds are lengthened; this conjugative effect is dependent on the conformation adopted by the π-acceptor with respect to the ring. For π-donors at C(3) (=O, =C, F_2 etc.) bond length asymmetry is reversed. In Part II[12] the X-ray data were used to examine the hybridization state of ring C atoms in **2**. It was shown that hybrid orbitals used in forming bonds to substituents have ~31% s-character ($sp^{2.22}$), while intra-annular hybrids are approximately $sp^{4.26}$ (19% s-character). Such results confirm the vinylic nature of **2**,[14] and are in good agreement with other experimental and theoretical findings.

Bonding effects in **2** can be formalized in terms of three essentially equivalent[15] models: the bent-bond model[16], the trigonally-hybridized (Walsh) scheme,[17] and the MO model.[18] Similar models (discussed below) can be applied to bonding in cyclopropene **1** and its derivatives **3**, **4**, **5**, **6**, and predict a somewhat acetylenic character for **1**, especially the 1,2-protons, in agreement with chemical knowledge.[2] Structural interest (both X-ray and gas-phase) in **1** has been slow, but a useful body of geometric data now exists. This data, for **1** and its derivatives, is examined in the present paper, particularly for effects of substitution on ring bond lengths and for evidence of rehybridization in intra- and extra-annular bonds. This study is greatly facilitated by comparison with analogous derivatives of **2**.

Bonding in cyclopropenes

The Walsh[17] and bent-bond[16] models for **1** are depicted in Fig. 1(a) and (b). In the Walsh[17] model the two vinylic C atoms are sp-hybridized, one p-orbital on each is then used in double-bond formation while the other contributes to the ring. The third ring C atom is sp^2-hybridized as in the cyclopropane model. Bernett[15] has shown that linear combinations of Walsh orbitals give rise to the Coulson & Moffitt bent-bond picture[16] of Fig. 1(b). The σ-framework of **1** is now formed from four $\sim sp^3$-hybrids (two at each vinylic C), with two $\sim sp^5$-hybrids at C(3) as in **2**. The C(1, 2) hybrids used to form bonds to substituents in **1** are now $\sim sp$ (in agreement with the chemically observed[2] acetylenic nature of the 1,2 protons), while "substituent" hybrids at C(3) are $\sim sp^2$ as in **2**. The MO picture of **1** is very similar to that of **2**[18,19] except that the AA-symmetry orbital of **2** has no counterpart in **1**.[20] Nevertheless all cyclopropane orbitals relevant to π-acceptor and π-donor interactions are present in **1**.[20]

[†] Parts I–III see Refs. 11–13.

Table 1. References to X-ray studies cited in this paper, ordered alphabetically by CCD reference code (see Text).

BZCPDC	Dimethyl 2,5-diphenyl-benzocyclopropene-1,1-dicarboxylate E.Carstensen-Oeser,B.Muller,H.Durr Angew.Chem., 84, 434, 1972
CBPAPD	cis-Dichloro-(tri-n-butylphosphine)-(bis(dimethylamino)-cyclopropenylidene)-palladium(ii) R.D.Wilson,Y.Kamitori,H.Ogoshi, Z.-I.Yoshida,J.A.Ibers J.Organomet.Chem., 173, 199, 1979
CHPRAN	(Cycloheptatrienylidene)-(2,3-diphenylcyclopropen-1-yl)-acetonitrile tetrafluoroborate C.Kabuto,M.Oda,Y.Kitahara Tetrahedron Lett., 4851, 1972
CLOFUL10	1,2,3,4-Tetrachloro-5,6-diphenylcalicene O.Kennard,K.A.Kerr,D.G.Watson,J.K.Fawcett Proc.R.Soc.London,Ser.A, 316, 551, 1970
CPCPRB	1,1-Dichloro-2,5-diphenylcyclopropabenzene B.Halton,T.J.McLennan,W.T.Robinson Acta Crystallogr.,Sect.B, 32, 1889, 1976
CPCPRO	bis(p-Chlorophenyl)-cyclopropenone K.Peters,H.G.von Schnering Chem.Ber., 106, 935, 1973
CPPCPD10	1,2,3,4-Tetrachloro-5,6-di-n-propylcalicene H.Shimanouchi,Y.Sasada,T.Ashida,M.Kakudo, I.Murata,Y.Kitahara Acta Crystallogr.,Sect.B, 25, 1890, 1969
CYANOF	2,3-Diphenyl-4,4-dicyanotriafulvene H.L.Ammon, J.Am.Chem.Soc., 95, 7093, 1973
CYANOF01	4,4-Dicyano-2,3-diphenyl-triafulvene N.B.Pahor,M.Calligaris,L.Randaccio, M.Lenarda, J.Chem.Soc.,Perkin 2, 130, 1979
MTFULC	1,2-Dimethyl-4,4-triafulvene-dicarbonitrile H.L.Ammon,C.Sherrer,T.Eicher Acta Crystallogr.,Sect.B, 34, 3782, 1978
MXCPCP	3,3-Di(methoxycarbonyl)-1-methyl-2-phenyl-cyclopropene C.Romming,A.S.Berg Acta Chem.Scand.Ser.A, 33, 271, 1979
NAPCPR	Naphtho(b)cyclopropene W.E.Billups,W.Y.Chow,K.H.Leavell,E.S.Lewis, J.L.Margrave,R.L.Sass,J.J.Shieh, P.G.Werness,J.L.Wood J.Am.Chem.Soc., 95, 7878, 1973
OMTHTC	3,3,7,7,10,10,14,14-Octamethyl-2,12-dioxo-5,12-dithiatricyclo(7.5.0.0(1,8))tetradeca-8-ene A.Krebs,R.Kemper,H.Kimling,K.-H.Klaska, R.Klaska Justus Liebigs Ann.Chem., 473, 1979
PCPCCR	Pentacarbonyl(2,3-diphenylcyclopropenylidene) chromium(0) G.Huttner,S.Schelle,O.S.Mills Angew.Chem., 81, 536, 1969
PCPNPY10	pi-(Triphenylcyclopropenyl)chloro-(dipyridine) nickel(0) pyridine solvate R.M.Tuggle,D.L.Weaver Inorg.Chem., 10, 2599, 1971
PCPRFE	Dicarbonyl-(eta(5)-cyclopentadienyl)-(1,2,3-triphenyl-cyclopropen-1-yl) iron R.Gompper,E.Bartmann,H.Noth Chem.Ber., 112, 218, 1979
PCPRNI10	pi-Cyclopentadienyl-pi-triphenylcyclopropenyl nickel R.M.Tuggle,D.L.Weaver Inorg.Chem., 10, 1504, 1971

CYPEPT	Triphenylcyclopropenium-bis(triphenylphosphine) platinum hexafluorophosphate benzene solvate M.D.McClure,D.L.Weaver J.Organomet.Chem., 54, C59, 1973
DMCPRP10	1,2,3-*tris(Dimethylamino)cyclopropenium* hexachlorodiplatinum C.D.Cowman,J.C.Thibeault,R.F.Ziolo,H.B.Gray J.Am.Chem.Soc., 98, 3209, 1976
DPCPRO10	2,3-Diphenylcyclopropenone monohydrate H.L.Ammon, J.Am.Chem.Soc., 95, 7093, 1973
DPCPRT	Diphenyl-cyclopropene-thione L.L.Reed,J.P.Schaefer J.Chem.Soc.,Chem.Comm., 528, 1972
DPCYPO	Diphenyl-cyclopropenone H.Tsukada,H.Shimanouchi,Y.Sasada Chem.Lett., 639, 1974
DPPTFE	Tetracarbonyl(diphenylcyclopropenethione) iron G.Dettlaf,U.Behrens,E.Weiss J.Organomet.Chem., 152, 95, 1978
FCPRPF	Ferrocenyl-diphenyl-cyclopropenium tetrafluoroborate R.L.Sime,R.J.Sime J.Am.Chem.Soc., 96, 892, 1974
MACPRP10	1,2,3-*tris(Dimethylamino)cyclopropenium* perchlorate A.T.Ku,M.Sundaralingam J.Am.Chem.Soc., 94, 1688, 1972
MCPRPT	3-Methyl-cyclopropene-bis(triphenylphosphine) platinum(0) J.J.de Boer,D.Bright J.Chem.Soc.,Dalton, 662, 1975
PHPRPC10	sym-Triphenylcyclopropenium perchlorate M.Sundaralingam,L.H.Jensen J.Am.Chem.Soc., 88, 198, 1966
PSMCPR	(+-)-3-(bis(Phenylsulfinyl)methyl)-1,2-dimethyl-cyclopropene H.Beckhaus,M.Kimura,W.H.Watson,C.G.Venier, B.Kojic-Prodic Acta Crystallogr.,Sect.B, 35, 3119, 1979
TCMSHD	1,2,3,3-Tetrachloro-4,5-dimethylspiro(2.3)hexa-1,4-diene R.J.Guttormson,B.E.Robertson Acta Crystallogr.,Sect.B, 29, 173, 1973
TMSCCO	1,6,6-Trimethyl-8-methoxycarbonylmethylspiro(2.5)oct-1-ene-7-one B.Frei,W.B.Schweizer,H.R.Wolf,O.Jeger Rec.J.R.Neth.Chem.Soc., 98, 271, 1979
TOFMFL	2,3-Di-p-tolyl-4,4-bis(trifluoromethyl) triafulvene H.L.Ammon,C.Sherrer,I.Agranat Chem.Scr., 11, 39, 1978
TPCPCQ	(eta(3)-Triphenyl-cyclopropenyl)-tricarbonyl-cobalt T.Chiang,R.C.Kerber,S.D.Kimball,J.W.Lauher Inorg.Chem., 18, 1687, 1979
TPCPRP10	1,2-Dimethyl-cyclopropene-bis(triphenylphosphine) platinum(0) J.J.de Boer,D.Bright J.Chem.Soc.,Dalton, 662, 1975

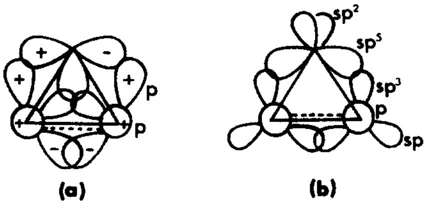


Fig. 1. (a) Walsh and (b) Bent-bond models of cyclopropene.

Methodology

The January 1981 release of the Cambridge Crystallographic Database (CCD) has been used to obtain relevant references to X-ray studies. Substructure searches, information retrieval and data analyses were performed using computer programs described by Allen *et al.*[21] and the approaches developed in earlier parts of this series.[11, 12] Each X-ray study is identified in this paper by the CCD reference code and the 34 relevant references, ordered alphabetically by this code, are in Table 1. Pertinent gas-phase data are included and referenced in the standard manner. Numbering schemes and designation of parameters follow Scheme 1. Error estimates for mean parameters ($\bar{x}$) are given by $\sigma(\bar{x}) = [\Sigma_n(\bar{x} - x_n)^2/n(n-1)]$ for n observations x_i ($i = 1, n$).

Geometry of free cyclopropene

Structural interest in cyclopropene and derivatives has been relatively slow. The first electron diffraction study[22] in 1952, and microwave work[24] in 1959 on **1** was not followed up until the 1970's. All 34 derivative X-ray studies have appeared since 1966, more than one-third in the past three years.

Gas-phase geometry for C_{2v}-symmetric **1** is collected in Table 2. Early work showed a short double bond (e.d. 1.29(4); mw 1.300 Å), while the single bond (e.d. 1.52(2); mw 1.515 Å) was not dissimilar to that in **2**. These results were confirmed by a recent extensive and accurate microwave study[25] which provides definitive parameters for discussion (Table 2).

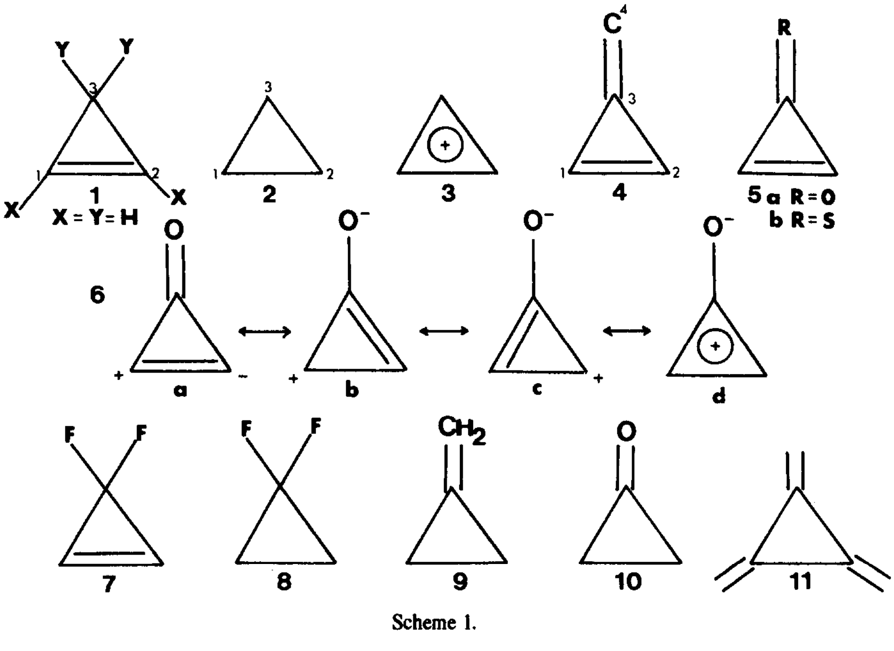
Intra-annular geometry[25] The 1-2 double bond of **1** is very short at 1.2959(4) Å, some 0.04 Å shorter than in ethylene,[28] and shorter even than the 1.3084(3) Å obtained for allene.[29] The comparable shortening in cyclopropane (C–C = 1.510(1) Å[11, 30]) relative to an unstrained C(sp^3)–C(sp^3) bond (1.533(2) Å[31]; 1.538(1) Å[12]) is only some 0.025 Å. The short value in **1** is due to increased *s*-character in the σ-component (~ sp^3 in **1**, *cf.* ~ $sp^{4.3}$ in **2**, together with strong pπ overlap.

The symmetry-equivalent single bonds in **1** at 1.509(1) Å[25] are, surprisingly, almost identical to the cyclopropane value (1.510(1) Å[11, 30]). A shorter distance might be expected from the bent-bond model (Fig. 1b) since the bond is formed from C(1)(sp³) and C(3)(sp^5) hybrids, rather than two ~ sp^5 hybrids in **2**. There are two explanations: overlap of ~ sp^5 and ~ sp^3 hybrids is poor *or* the C(1) ring hybrid is close to sp^5 as in **2**. The latter implies that the C(1) hybrid used in double-bond formation is closer to sp^2 than sp^3, thus providing a convenient rationale for the short 1–2 distance in **1**. Data for the 3,3-difluoro derivatives of **1** and **2** indicate, however, that the former explanation is more probable and the expected shortening of 1–3, 2–3 to 1.48–1.49 Å is not achieved. This point is further discussed below.

Only one X-ray study (TMSOCO) has a cyclopropene ring with only C(sp^3) and H substituents. Ring geometry (Table 2) is in good agreement with gas-phase data.

Extra-annular bonds. The methylenic H–C(3)–H angle and C(3)–H bond length (114.6(2)°, 1.088(2) Å[25]) confirm the vinylic nature of the C(3) protons in **1**. Comparable values for **2** are 115(1)° and 1.089(3) Å.[30] Data for C(3)–C(sp³) substituted cyclopropenes are sparse. Four X-ray values range from 1.514 to 1.549 Å (mean 1.53(1) Å), while the microwave value is 1.52(1) Å. The mean value of 146 C(ring)–C(sp^3) bonds in cyclopropane is 1.519(2) Å.[12]

The formally vinylic C(1, 2)–H bond of 1.072(1) Å in **1**[25] is short and implies[2] some 42% *s*-character in the C(1, 2)-substituent hybrid. Similar observations apply to 1-methylcyclopropene where C(1)–C(Me) is 1.476 Å.[27]



Scheme 1.

Table 2. Gas-phase data on cyclopropene and its simple derivatives.

Compound	Ref	Expt	X	Y	D12	D13	D1X	D3Y	A132	A123	A12X	AY3Y
Cyclopropene 1	22	ED	H	H	1.29(4)	1.53(2)	1.09(4)	1.09(4)	49.9	65.1	152.0	118.0*
1	23	ED	H	H	1.305(3)	1.521(2)		1.11(2)	50.8	64.6		
1	24	MW	H	H	1.300	1.515	1.070	1.087	50.8	64.6	149.6	114.7
1	25	MW	H	H	1.2959(4)	1.509(1)	1.072(1)	1.088(2)	50.84(5)	64.58	149.85(8)	114.57(19)
3,3-Dimethyl-1	26	MW	H	Me	1.294(10)	1.52(1)	1.07*	1.52(1)	50.4	64.8	149.9*	114(1)
1-Methyl-1	27	MW	Me	H	1.300*	1.515*	1.476	1.09*	50.8*	64.6	152.5	114.7*
TMSOCO		X	Me	Cr	1.284(3)	1.503(2)	1.469(2)	1.528(3)	50.7(1)	64.7(1)	150.9(1)	110.9(2)

Notes : ED = Electron Diffraction; MW = Microwave; X = X-ray; Me = Methyl; Cr = Ring carbon Geometry refers to formula 1 of Scheme 1. Error estimates are in parentheses, assumed values are marked with an asterisk.

There are seven independent C(1, 2)–C(sp^3) bonds in the organic X-ray literature, all R-factors are <0.08 and the mean bond length is 1.477(6) Å. Using bond length "calibration" points established earlier[12] an estimate of 45.6% s-character ($sp^{1.19}$) is obtained for the C(1) hybrid. This result is in agreement with Walsh and bent-bond models (Fig. 1), and the known[2] acetylenic nature of the 1,2-protons in 1.

Cyclopropenium ion

Structural data for cyclopropenium ion 3 is considered here since its geometry is relevant to the discussion of cyclopropenylidene derivatives (4, 5) which follows. Cyclopropenium ion, stabilized by suitable substituents, (e.g. phenyl, dimethylamino, n-propyl) is one of the few carbonium ions for which X-ray data are available. Relevant geometry, primarily for triphenyl derivatives, is in Table 3. There are three studies of the uncomplexed ion and three having symmetric π-coordination involving Ni and Co.

Cyclopropenium ion represents the simplest Hückel system, with two delocalized π-electrons. In the bent-bond model (Fig. 1b) *each* C atom contributes two $\approx sp^3$ hybrids to the σ-framework, with one $\sim sp$ hybrid involved in substituent bonds as in 1. Table 3 confirms the expected D_{3h}-symmetric aromatic structure. Mean ring-bond lengths range from 1.363(7) to 1.384(8) Å in uncomplexed ions, with an overall mean of 1.373(3) Å. Variations among structures are marginally significant at these accuracy levels but it is suggested (MACPRPIO, Table 1) that the shorter 1.363(7) Å value in this structure may reflect stronger electron donation from N(Me)$_2$ than from phenyl in PHPRC10.

The mean C–C bond in 3 is thus 0.024 Å shorter than in benzene. This result is perhaps surprising, since the double bond in 1 was foreshortened by 0.04 Å compared to ethylene. However, with 2π electrons, each bond in 3 has 33% double bond character, rather than the 50% in benzene. Pauling[32] gives a comparative unstrained distance of 1.415 Å(wt%) for one third double bond character, some 0.043 Å longer than in 3. It is also interesting to note that, assuming the C-substituent hybrid in 3 to have ~45% s-character (as at C(1,2) in 1), then the σ-framework of 3 is formed from sp$^{2.64}$ hybrids (27.5% s) for which an interorbital angle of 112° may be calculated[33]. In the construction of Fig. 2 we may calculate an "arc" or "bent" bond length of 1.421 Å, marginally longer than the unstrained comparator 1.415 Å. This result should be compared with data for cyclopropane where an interorbital angle of 103.6° yields an arc bond (Fig. 2) of 1.547 Å, again marginally longer than unstrained C(sp^3) – C(sp^3) distances.

Bonds to substituent phenyl groups which lie within 15° of coplanarity with the 3-membered ring, range from 1.416(9) to 1.435(9) Å with a mean of 1.422(5) Å. This is very short by comparison with the 1.488(3) Å obtained from analysis of a number of biphenyls in the CCD. Such a comparison is somewhat dubious, however, due to intermolecular overcrowding in many biphenyls. Hence the phenyl-C=C system was analysed, via CCD, using techniques described by Allen[12] to give a mean phenyl-C=C bond of 1.459(3) for 23 conjugated systems, and 1.477(6) Å for 37 systems having unfavourable orbital overlap. Similar studies of phenyl-C≡C and C=C–C≡C substructures gave 1.437(3) and 1.431(2) Å for the single bond over 31 and 12 occurrences respectively. The short cyclopropenium-phenyl distances therefore imply a C(ring) hybrid very close to sp, together with considerable stabilizing delocalization over the whole system. An equivalent alternative description, in line with that of Pauling,[32] is afforded by noting that the 1.422(5) Å average implies *ca.* one-third double bond character in the substituent bond (which is almost equal to the arc bond calculated above). Thus there is extensive resonance stabilization of the substituted system. Similar conclusions can be drawn from the short (1.333 Å) C(ring)-N bonds in MACPRP10. The C(ring)-phenyl distances appear to depend on the ring-phenyl interplanar angle, the shortest distances corresponding to near coplanarity (Table 3).

In π-coordinated complexes of 3, where the metal adopts a symmetric disposition, the mean C–C distance increases, as expected, to 1.426(3) Å, and D_{3h}-ring symmetry is preserved. A very recent study[34] has C–C(ring) = 1.41(1), C(ring)-phenyl = 1.47(1), and Ni–C(ring) = 2.03(1) Å, in excellent agreement with Table 3. Other organometallic compounds of 1 and 3 are discussed below.

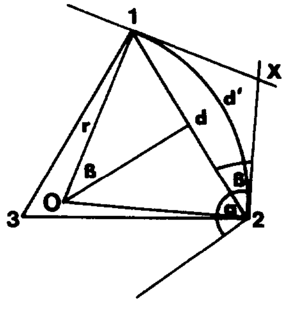


Fig. 2. Calculation of the 'arc' or 'bent' bond (d'). For an inter-orbital angle α, $\beta = (\alpha - 60)/2$. (d') is the arc of the circle of centre O having radius $r = d/(2 \sin \beta)$. Hence: $d' = 2\pi\beta d/360 \sin \beta$.

Table 3. X-ray geometry for cyclopropenium derivatives

Refcode	Subst.	R	<σ>	D1	D2	D3	<D>	D1s	D2s	D3s	A1s	A2s	A3s	
Organic Derivatives of **3**														
PHPRPC10	Ph Ph Ph	0.075	9	1.369	1.376	1.374	1.373	1.459	1.435	1.416	21.2	12.2	7.7	
MACPRP10	Nm Nm Nm	0.076	7	1.363	1.363	1.362	1.363	1.326	1.337	1.337	9.9	20.8	20.8	
PCPRPF	Ph Ph Cp	0.057	8	1.391	1.385	1.376	1.384	1.417	1.422	1.445	7.5	11.2	14.6	
Symmetrical pi-complexes of **3**														
PCPNPY10	Ph Ph Ph	0.081	11	1.414	1.428	1.422	1.421	1.461	1.455	1.459	20.1	25.2	18.3	Ni-C=1.941(5)
PCPRNI10	Ph Ph Ph	0.056	8	1.439	1.428	1.422	1.430	1.451	1.438	1.466	26.9	31.7	29.3	Ni-C=1.961(4)
TPCPCQ	Ph Ph Ph	0.045	5	1.430	1.425	1.422	1.426	1.447	1.474	1.461	35.3	14.4	26.3	Co-C=2.01(1)

Notes : Subst.= Substitution pattern; R = Crystallographic R-factor; <σ> = Mean e.s.d. (x10**3) for bonds. <D> = mean bond length in cyclopropenium ring; Dns (n=1,2,3) = C(ring) - substituent bond length; Ans (n=1,2,3) = Dihedral angle between cyclopropenium ring and mean plane through substituent. Substituents : Ph = Phenyl; Nm = Trimethylamino; Cp = Cyclopentadiene.

Cyclopropenylidene derivatives and other π-donor substituted cyclopropenes

The majority of the organic X-ray literature for **1** refers to rings having exocyclic double bonds at C(3) i.e. methylenecyclopropene (triafulvene, **4**), cyclopropenone **5a** and cyclopropenethione **5b**. Relevant geometry is collected in Table 4. All X-ray studies are of 1,2-diphenyl derivatives of **4**, **5**, excepting CPPCPD10 and MTFULC which have 1,2-di-C(sp^3) substitution. All examples of **4** have two additional unsaturated (and conjugated) groupings at C(4), except for TOFMFL, which has 4,4-bis(trifluoromethyl) substitution. Interest in cyclopropenylidenes centres around the extent to which dipolar and fully delocalized resonance hybrids **6** contribute to ground state structures of **4**, **5**. Evidence for significant resonance contributions comes from spectroscopic studies, dipole moments and some MO calculations.[2,8,35,36] In this context, and to preserve an analogy with earlier work on **2**,[11] relevant data for other π-donor (halogens, e.g. **7**) derivatives of **1** (primarily gas-phase results) are collected in Table 5. Data for analogous derivatives of **2** (e.g. **8–10**) are also in Table 5 for comparison purposes.

1,2-Di-C(sp^3) derivatives. Both CPPCPD10 and MTFULC (Table 4) have two conjugative substituents at C(4) in **2**. The 1–2 double bond [1.323(4) Å] is 0.027 Å longer than in **1** and 0.021 Å longer than in cyclopropenone **5a**.[37] The mean ring single-bond is very short at 1.391(1) Å, only 0.018 Å longer than in cyclopropenium ion **3**. It is 0.067 Å shorter than the 1.458(3) Å obtained for conjugated C=C–C=C systems[12] and 0.118 Å shorter than single bonds in **1**.[25] This distal bond lengthening and vicinal shortening is reminiscent of π-donor effects in **2**.[11] The 1–3 distance in **4**, **5** is important in assessing the significance of contributions from **6** and is more fully discussed below.

The exocyclic 3–4 double bond in CPPCPD10 and MTFULC is long at 1.368(1) Å, but consistent with other data in Table 4. It is longer than the 1.335(2) in tetracyanoethylene[43] and comparable with the 1.374(3) Å in neutral tetracyanoquinodimethane.[44] The lengthening is due to conjugation with C(4)-substituents and to significant π-donation to the ring (see below).

1,2-Diphenyl derivatives. Here the 1–2 double bond of **4**, **5** is further lengthened, by 0.025 Å, to 1.348(2) Å. This seems reasonable by comparison with planar trans-stilbene[45] where C=C is 1.338(2) Å, an increase of 0.016 Å over values obtained for C=C in the C(sp^3)–C=C–C(sp^3) system.[12] The 1–3 ring bonds, although still short, are 0.017 Å longer than in CPPCPD10 and MTFULC above. These results, together with a mean C(1, 2)-phenyl bond of 1.445(3) Å (phenyls within 15° of coplanarity with central ring), indicate some ring-phenyl conjugative interaction. The ring-phenyl bond, although 0.023 Å longer than for **3**, still indicates a C(1, 2) hybrid close to *sp*. Exocyclic methylenes all carry two additional conjugative substituents except for TOFMFL [bis(trifluoromethyl)]. The mean conjugated 3–4 distance is 1.367(4) Å; the 1.357(7) Å in TOFMFL is only marginally shorter and the overall mean, 1.365(4) Å, is cited in Table 4.

Other π-donors. The parent cyclopropenone **5a** has been studied by microwave spectroscopy.[37] Geometry (Table 5) shows a 1–2 double bond only marginally longer than in **1** but the shortening of 1–3 to 1.412(3) Å agrees with the X-ray data of Table 4. While a longer 1–2 bond might have been expected for **5a**, it is possible that stabilizing electronic interactions with 1,2-C(sp^3) substituents may contribute to the lengthening in CPPCPD10 and MTFULC (Table 4, see above). Such an explanation is based on the unusual stabilization of **3** by trimethyl and tri-*n*-propyl groups.[2,45] More data on **5a** and derivatives is required to settle this point.

The dramatic effect of 3,3-difluoro substitution on cyclopropane **2** has been discussed.[11] The distal bond in **8** increases to 1.553(2) Å and the vicinal bonds shorten to 1.464(2) Å[42] (Table 5). The effect of 3,3-dichloro substitution on **2** is smaller.[11] A similar effect is observed in 3,3-difluorocyclopropene **7**[38] with the distal bond lengthened to 1.321(1) and the vicinal bonds shortened to 1.438(7) Å by comparison with **1**.[25] In **7**[38] the F–C–F angle closes to 105.5(5)°, compared to 114.6(2)° in **1**.[25] This implies that *all* C(3) hybrids are closer to sp^3. The same trend is observed in **8**[42] and **2**.[30] In perchlorocyclopropene[39] the 1–2 bond is 1.32(1) and 1–3, 2–3 bonds are 1.48(1). The C(3)–Cl distance of 1.771(4) Å is much longer than C(1, 2)–Cl [1.684(4) Å], with Cl–C–Cl = 108.8(4)°. Such data indicate C(1, 2) hybrids of ~ *sp* and almost symmetric sp^3 hybridization at C(3).

Resonance contributors - or not? The spectroscopic, dipole moment and MO theoretical evidence[2,8,35,36] for resonance contributions from dipolar and aromatic forms **6** to ground states of **4**, **5** is somewhat inconclusive. The arguments may be summarised briefly as: (i) Chemical shifts of ring protons in **5a** and in its 1-*n*-propyl, 1-methyl and 1-*n*-pentyl derivatives (mean $\delta = 8.72$) lie between values for (**1**, $\delta = 6.66$) and (**3**, $\delta = 10.42$), but no account is taken of magnetic anisotropy of the C=O group.[8]

(ii) Dipole moments for 1,2-diphenylcyclopropenone are reported as 5.08 – 5.14 D, with 4.78 D for 1,2-di-*n*-propylcyclopropene,[8] the value for **1** itself is only 0.454 D.[24] Ammon[35,36] argues that the increase is not solely a function of charge separation (the explanation of Tobey[47] based on the 2.89 D moment for acetone) and presents CNDO/2 results which show an increase in charge magnitude as well as separation.

(iii) Pahor *et al.*[48] have used a Walsh orbital model for **4**, **5** to predict a significant contribution by pseudoaromatic **6d**.

The most striking structural feature in Tables 4 and 5 is the very short 1–3 distance in **4**, **5**, and **7**. In **4**, **5** the range is 1.390(2)–1.419(3) with a mean of 1.405(3) Å which will be used in the ensuing discussion. This mean is an almost exact average of the double (mean = +0.109 Å) and single (– 0.104 Å) bonds in **1**,[25] and is only 0.032 Å longer than the bond length in aromatic **3**. By comparison with unstrained systems it is 0.053 Å shorter than the 1.458(3) Å obtained for the single bond in conjugated C=C–C=C systems.[12] Thus the 1.405(3) Å value might be taken to indicate significant resonance contributions from **6b**, **c**.

The structural evidence of **1**, **4**, **5** should, however, be interpreted in conjunction with data for analogous derivatives of **2**. In methylenecyclopropane **9**[41] the vicinal bonds [1.457(1) Å] are 0.053 Å shorter than in the parent **2**[30] and 0.050 Å shorter than unstrained C(sp^2)–C(sp^3) single bonds.[12] Such shortening is a consequence of the π-donor effect on the ring σ- and π-electron distributions,[49] which also produces a lengthening of distal bonds. Since the relevant orbitals of **2** are also present in **1**,[20] a similar effect is expected for **1**;[49] indeed the 1–2 double bonds in Tables 4 and 5 are all lengthened with respect to the 1.2959(4) Å in **1**,[25] with the possible exception of cyclopropenone **5a**.[37] Similar arguments can be applied to compare **10** and **5a**.

Further 1–3 bond shortening in **4**, **5** may also be

Table 4. X-ray geometry for cyclopropenylidene derivatives.

Refcode	R3	R1,2	R	<σ>	D12	D23	D13	A3	A1	A2	DR3	DR1	DR2	A1s	A2s	A21s	A12s
CHPRAN	C	Ph	0.080	9	1.353	1.398	1.398	57.8	60.9	61.3	1.380	1.430	1.443	6.5	27.0		
CLOFUL10	C	Ph	0.057	10	1.349	1.419	1.406	57.0	61.0	62.0	1.356	1.432	1.460	0.5	45.1	146.1	146.4
CYANOF	C	Ph	0.035	3	1.344	1.398	1.398	57.5	61.3	61.3	1.366	1.444	1.444	5.9	5.9	151.3	151.3
CYANOF01	C	Ph	0.047	4	1.351	1.400	1.400	57.7	61.2	61.2	1.366	1.448	1.448	5.8	5.8	151.1	151.1
TOFMFL	C	Ph	0.073	7	1.340	1.418	1.413	56.5	61.6	61.9	1.357	1.441	1.450	4.7	4.0	148.9	150.0
Mean(**4**, R1,2 = Ph)					1.347(2)	1.406(3)		57.5(2)	61.4(1)		1.365(4)	1.441(3)					
DPCPRO10	O	Ph	0.043	4	1.351	1.404	1.414	57.3	61.7	61.0	1.230	1.453	1.455	7.9	2.4	150.0	148.5
					1.356	1.411	1.410	57.5	61.2	61.3	1.220	1.453	1.449	4.2	10.5	149.5	149.4
DPCYPO	O	Ph	0.095	10	1.349	1.415	1.418	56.9	61.4	61.7	1.225	1.438	1.455	2.1	2.3	149.7	151.5
Mean(**5a**, R1,2 = Ph)					1.352(2)	1.412(3)		57.2(2)	61.4(1)		1.225(3)	1.451(3)					
DPCPRT	S	Ph	0.100	10	1.338	1.403	1.403	57.0	61.5	61.5	1.630	1.440	1.440	4.0	4.0		
Mean(**4**,**5a**,**5b**, R1,2 = Ph)					1.348(2)	1.408(2)		57.2(2)	61.4(1)			1.445(3)					
CPPCPD10	C	Pr	0.073	9	1.320	1.390	1.390	56.7	61.7	61.6	1.370	1.466	1.466			149.6	152.4
MTFULC	C	Me	0.041	3	1.327	1.391	1.394	56.9	61.5	61.6	1.366	1.458	1.478			151.0	150.8
Mean(**4**, R1,2 = C(sp3))					1.323(4)	1.391(1)		56.8(1)	61.6(1)		1.368(1)	1.467(2)					

Notes : n = 1,2,3 refer to formulae **4**, **5a**, **5b** in Scheme 1; Rn identifies substituents; Dnm are bond lengths; An are internal angles in the three-membered ring; DRn are ring to substituent distances; Ans are dihedral angles (as in Table 3); Anms are external valence angles to substituents. For R and <σ> see Table 3. Mean values are calculated assuming mirror symmetry in the three-membered ring.

Table 5. Gas-phase geometry for π-donor derivatives of cyclopropene (1) and cyclopropane (2).

Compound	No.	Ref	D12	D13	A3	A1	D3s	As3s
Cyclopropene	**1**	25	1.2959(4)	1.509(1)	50.84(5)	64.58	1.088(2)	114.6(2)
Cyclopropenone	**5a**	37	1.302(3)	1.412(3)	55.0(3)	62.5(3)	1.212(2)	-
3,3-Difluoro-1	**7**	38	1.321(1)	1.438(7)	54.6(4)	62.7(4)	1.365(5)	105.5(5)
Perchloro-1		39	1.320(10)	1.479(10)	53.0	63.5	1.771(4)	108.8(10)
Cyclopropane	**2**	30	1.510(2)	1.510(2)	60.0	60.0	1.089(3)	115(1)
Methylene-2	**9**	41	1.5415(3)	1.457(1)	63.8	58.1	1.332(1)	-
Cyclopropanone	**10**	40	1.575(12)	1.475(20)	64.6(9)	57.7(4)	1.191(20)	-
3,3-Difluoro-2	**8**	42	1.553(1)	1.464(2)	64.1(1)	57.9	1.355(2)	108.3(2)

Notes : Distances in A, angles in degrees, error estimates in parentheses. All data are from microwave work except for 2 (electron diffraction). The ring has C(2v)-symmetry, hence D13 = D23, A1 = A2. D3s is the ring C(3) to substituent bond length, As3s is the valence angle between geminal substituents at C(3).

expected from rehybridization at C(3). The bent-bond model (Fig. 1b) shows that C(3) should have ~ sp^3 intra-annular hybrids in **4**. This provides stronger σ-overlap and should foreshorten 1-3 in **4**, **5** before additional shortening due to π-donation. These arguments all imply that the basic 1-3 distance of 1.509(1) Å in **1**[25] is a bad comparator, as suggested to the discussion of Table 2 above. Additional evidence for this is provided by the gem-dihalide data of Table 5. In 3,3-difluorocyclopropane **8**[42] the vicinal bonds shorten by 0.046 Å compared to **2**, in 3,3-difluorocyclopropene **7**[38] the shortening is 0.071 Å. Since the orbital structures[19] of **1** and **2** are similar, the additional shortening (0.025 Å) may be assigned to improved σ(1-3) overlap in **7**. Similar trends are observable in perchlorocyclopropene,[39] although analysis is complicated by the additional 1,2-dichloro substitution. In both cases F–C–F and Cl–C–Cl angles are close to tetrahedral (Table 5) and imply sp^3 hybridization at C(3). Thus the 1.509(1) Å[25] single bond in **1** is most likely due to poor sp^5–sp^3 overlap (see above) and a value of ~ 1.484 Å is suggested here as a suitable comparator for **4**, **5**. Results for trimethylenecyclopropanes **11**[50,51] support this view and indicate that 1.484 may be over-estimate. In **11** π-donor effects should cancel according to the additivity postulate;[20,11] the D_{3h}-symmetry averaged bond length is 1.452(2) Å. Even accepting that this bond is foreshortened by ~ 0.025 Å due to normal conjugation[12] a basic 1-3 bond of ~ 1.477 Å is indicated.

The effects of rehybridization and π-donation will therefore combine to shorten the 1-3 distance in **4**, **5** by as much as 0.085 Å giving a bond of 1.424 Å. This would support the view that resonance contributions from dipolar **6b**, **6c** are small, and are very unlikely from **6d**, especially since the effects of cross-conjugation[52] are not included above. This conclusion conflicts with the work of Ammon[35,36] and Pahor *et al.*[48] It is supported, however, by an analysis of magnetic susceptibility anisotropies,[37] which show no appreciable ring current in **5a** (thus excluding pseudoaromatic **6d**) and by recent *ab initio* work[53,54,55] which indicated **6a** as the only realistic contributor.

π-Acceptor derivatives of cyclopropene and benzocyclopropenes

The three X-ray studies of organic cyclopropenes having only π-acceptor, C(sp^3) and H substituents (MXCPCP, OMTHTC, TCMSHD) are discussed here, together with three benzo- and naphthocyclopropenes (BZCPDC, CPCPPB, NAPCPR), since the two groups have some common features. The sparse data is not directly comparable, hence relevant substructural geometry is displayed in Fig. 3, rather than tabulated.

For 'π-acceptors' at C(3) the ring double bond is slightly shorter than the microwave value for **1**,[25] and almost identical to the X-ray value in TMSOCO (Table 2). Bonds vicinal to the acceptor in MXCPCP and OMTHTC are, however, longer than the 1-3 distance in **1**.[25] This is reminiscent of the conjugative effect in cyclopropane,[11] although torsion angles O=C–C(3)–X (X is the mid-point of distal bond[11]) are at the limit established for effective orbital interactions. Conjugation is shown more clearly in the benzocyclopropene BZCPDC, which exhibits the shortest (distal) fusion bond of Fig. 3(d)–(f) and the longest vicinal bonds. Unfortunately coordinate data is unpublished, so conformational angles cannot be calculated. TCMSHD does not follow trends identified above, probably due to rehybridization at the spiro atom. The structure is best compared with that of spiropentane (Fig. 3g) studied by microwave methods.[56]

Benzocyclopropenes have already been discussed[13] in terms of the angular deformations in the benzene ring induced by small-ring fusion. This study[13] also showed no structural evidence for double-bond fixation in benzene as predicted by Mills and Nixon.[57] CPCPRB exhibits the expected shortening of cyclopropene single bonds due to rehybridization and π-donation by the *gem*-dichloro substituents, the distal fusion bond here is significantly longer than in BZCPDC, in line with π-donor perturbation. Cyclopropene single bonds in NAPCPR are very similar to those in **1**[25] and TMSOCO (Table 2), while the fusion bond length approaches the value for aromatic **3**. The angular deformation pattern in the naphthalene nucleus differs from that in benzene,[13] and is presently being studied.[58]

Organometallic derivatives of cyclopropene

Three major bonding patterns are exhibited in available structures of organometal-cyclopropenes: (i) symmetrically π-coordinated cyclopropenium rings, (ii) unsymmetric π-coordination of cyclopropene and cyclopropenium, and (iii) σ-bonded complexes of **1** and **3**. Category (i) is discussed above and relevant data are in Table 3.

CYPEPT and TPCPRP10 (Table 1) have type (ii) bonding. In both structures Pt is almost equidistant from two ring C atoms with Pt–C in the narrow range 2.09(2)–2.12(1) Å. The third C atom is 2.48(2) and 2.83(1) Å from Pt in CYPEPT and TPCPRP10 respectively. The ring

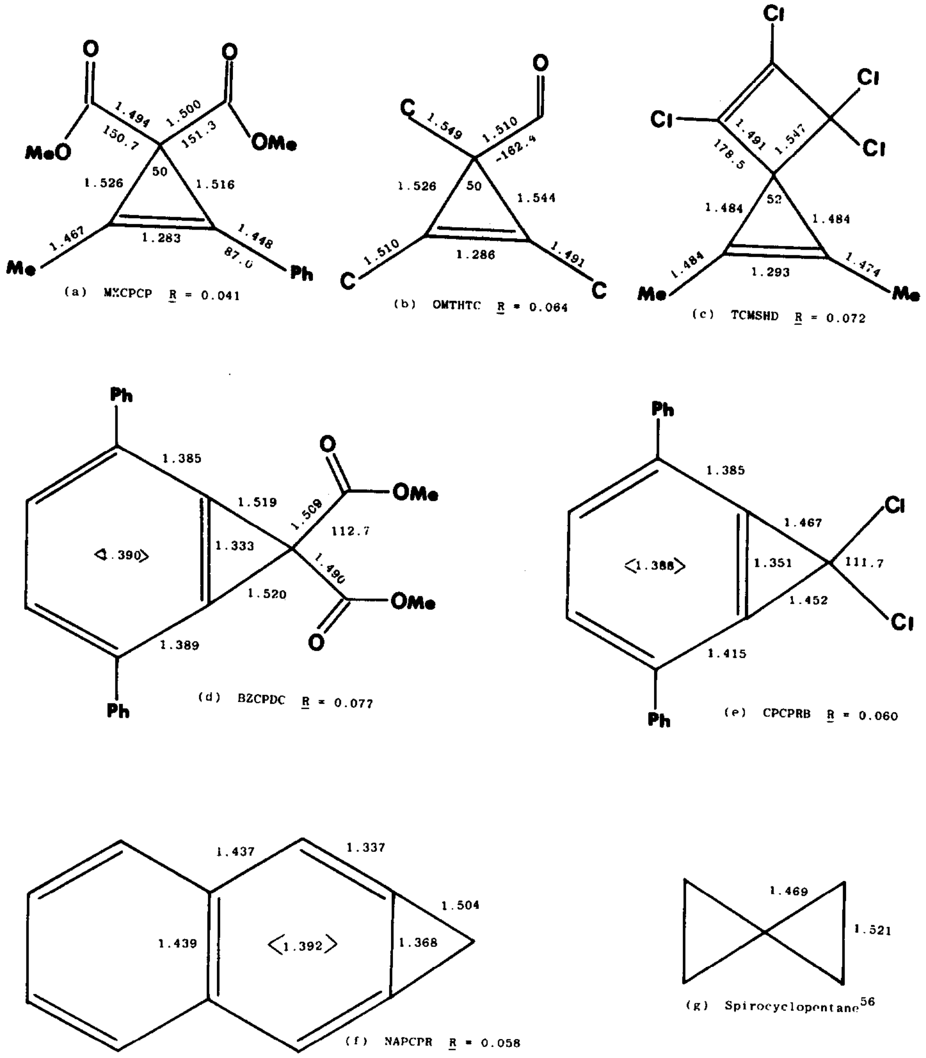


Fig. 3. π-Acceptor and π-donor derivatives of cyclopropene and benzocyclopropene. (Bond lengths in Å, angles in degrees). Comformational angles for π-acceptors (see text) are given where available.

C–C distances, however, are quite different: 1.58(2), 1.38(2), 1.40(2) in CYPEPT and 1.50(1), 1.55(1), 1.54(1) in TPCPRP10 (coordinated bond cited first). Both compounds are best regarded as Pt(0)–olefin complexes, and the lengthening of the coordinated C–C bond indicates that CYPEPT is a complex of 3 while TPCPRP10 is a complex of 1.

CBPAPD, PCPCCR and PCPRFE are σ-bonded (type iii) complexes of Pd, Cr and Fe respectively. In CBPAPD and PCPCCR ring C–C distances are all in the narrow range 1.350–1.400 with respective means of 1.382 and 1.380 Å, indicating aromaticity. Ring bonding in PCPRFE is localized as in 1 with 1 − 3, 2 − 3 = 1.506, 1.516 Å and 1 − 2 = 1.291 in good agreement with results in Table 2; Fe is bonded to C(3) of 1. In all cases the C-metal distances (1.961, Pd, CBPAPD, 2.05, Cr, PCPCCR; 2.079 Å, Fe, PCPRFE) all indicate some degree of double bond character.

DPPTFE is a tetracarbonyliron complex of cyclopropenethione **5b** with Fe–S bonding. The geometry of the **5b** moiety is almost identical to that of DPCPRT (Table 4).

Summary

This paper reviews the available X-ray and gas-phase geometries of cyclopropene **1** and its derivatives, including cyclopropenium ion **3** and cyclopropenylidenes **4**, **5**. The work mirrors recent reviews of the saturated analogue cyclopropane **2**[11,12] and compared ring geometries where possible. Data on cyclopropenes is quite sparse, but the following conclusions may be drawn:

(i) The bent-bond model[16] (Fig. 1b) provides a reasonably accurate description of **1**. Geometrical data indicate that C(1, 2) use $sp^{1.19}$ hybrids to form bonds to substituents (sp in Fig. 1b). The C(1, 2) ring σ-hybrids are then $sp^{2.68}$ (sp^3 in Fig. 1b). Ring and substituent hybrids at C(3) are assumed to be as in **2**,[12] *i.e.* $sp^{4.26}$ and $sp^{2.22}$ respectively. Poor overlap of $sp^{4.26}$ and $sp^{2.69}$ hybrids may account for the unexpectedly long 1-3 single bond of 1.509(1) Å[25] (*see* 1.510(1) Å[11,30] for $sp^{4.26}$-$sp^{4.26}$ in **2**).

(ii) Cyclopropenium ion **3** has a D_{3h}-symmetric ring with a mean bond length of 1.373(3) Å, a value that can be related to distances in unstrained systems.

(iii) Short intra-ring single bonds in cyclopropenylidenes **4**, **5** do not indicate extensive resonance contributions from **6**. The π-donor effect observed for **2**[11,20,48] operates in **4**, **5** and in the difluoro compound **7**. Vicinal bond shortening is very apparent, while additional shortening is attributable to rehybridization at C(3).

(iv) Insufficient data exists to quantify the effect of π-acceptors[11] on **1** but some lengthening of vicinal bonds is observed.

(v) Organometallic derivatives of **1** and **3** are formed and three major bonding patterns are identified.

(vi) C–C distances in unstrained molecules are inadequate comparators for distances in three-membered carbocycles, where the orbital structure permits 'anomalous' electronic effects.

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