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THE GEOMETRY OF SMALL RINGS—V

GEOMETRIC VARIATIONS AND HYBRIDIZATION IN THREE-MEMBERED HETEROCYCLES C_2X (X=N, O, Si, P, S) AND CXY (X, Y=N, O)†

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Abstract—Structural data relating to 369 organic derivatives of C_2X(X=N, O, Si, P, S) and CXY(X, Y=N, O) heterocycles have been retrieved from the Cambridge Crystallographic Database and analysed in conjuction with pertinent gas-phase results. Heterocycle geometries are compared with each other, and with those for the 'parent' carbocycles cyclopropane and cyclopropene. For saturated C_2X rings the previously observed (gas phase) decrease in C–C bond length (d_{cc}) and bent-back angle (γ) with increasing heteroatom electronegativity (χ_x) are confirmed as linear relationships using mean solid state geometry for X=C, N, O, S. The C–X bonds show an effective increase in length with increasing χ_x, in line with their facile cleavage in ring opening reactions. A model for hybridization changes at C in saturated C_2X rings is derived empirically and is in broad agreement with theoretical studies. There is no evidence for geometric variations in the heterocyclic rings induced by π-acceptor substituents, but π-donor substituent effects are directly comparable to those occurring in cyclopropane and cyclopropene. Geometric variations in unsaturated heterocycles are analogous to those in cyclopropene derivatives; C–C double bond lengths in available C_2X systems appear to indicate a χ_x dependence. Heteroatom-heteroatom bonds in CXY systems are weak, with N–O weaker than N–N, in agreement with thermochemical reasoning.

Mono- and di-hetero analogues of cyclopropane (Table 1 which includes C_2X and CXY rings for which geometry is available) have characteristically high strain energies.[1] Derivatives of some rings have only recently been prepared, while other C_2X, CXY systems have never been observed, even spectroscopically. The presence of a heteroatom, coupled with the strain in the system, makes the rings highly reactive: carbon-heteroatom and (especially) the heteroatom-heteroatom bonds are weak, by comparison with unstrained systems, and both electrophiles and nucleophiles initiate facile ring-opening reactions.[1]

Bonding in C_2X and CXY rings may be compared in simple terms with that in cyclopropane (**1**) or cyclopropene (**7**). Ring σ-bonds are bent[2] with electron-density maxima lying outside the C–C, C–X vectors (*cf* the bonding electron density distributions for **1**[3,4] with those for **2**[5]). The rationalizations of Bernett[6] then indicate increased *s*-character in the C-hybrids used in forming bonds to substituents, with a consequent reduction in *s*-character for ring σ-hybrids. Earlier geometric analyses indicate C-substituent hybrids of $\sim sp^{2.22}$ in **1**[7] and $\sim sp^{1.19}$ in **7**,[8] and σ-hybrids of $\sim sp^{4.26}$ in **1**[7,8] and $\sim sp^{2.68}$ in **7**.[8]

It is known, however, that the introduction of heteroatoms into small rings produces significant variations in molecular geometry which reflect the changes in covalent radii and effective hybridizations. Earlier spectroscopic studies of **1**,[9] **2**,[10] and **3**[11] showed that the C–C bond length [1.524(14), 1.480(–), 1.472(2)Å in **1**, **2**, **3** respectively] was related to heteroatom electronegativity. Such geometric perturbations of C_2X rings have been analysed[12–14] in terms of the interaction of a heterogroup (X=CH_2, NH, O, SiH_2, PH, S) with ethylene. This approach is directly analogous to bonding models proposed for transition metal–ethylene complexes[15,16] which result in the formation of metallacyclopropanes. Fig. 1 shows that two mechanisms operate: (i) electron donation from a suitable heterogroup orbital into ethylene π^*, and (ii) donation from ethylene π into heterogroup orbitals, including *d*-orbitals where available. Both mechanisms yield a lengthening of the ethylenic link, a bending of the olefin substituent plane (CZZ′ in Fig. 2) out of the ethylenic plane, and a destabilization of the σ-framework. For main group C_2X rings mechanism (i) predominates so that the C–C bond length and the "bent-back" angle (γ in Fig. 2) both decrease as the donor ability of X decreases, i.e. as the electronegativity of X increases. A linear relationship between γ and the C–C distance has been observed[17] in metallacyclopropanes, while Delker *et al.*[14] have found that a similar relationship is approximated by microwave data for **1–6** (X-ray for **4**) and have also correlated the C–C distance with electronegativity.

The present paper uses predominantly X-ray results, augmented by pertinent gas-phase data, to re-examine the electronegativity relationships for saturated C_2X rings. The analysis is extended to a comparison of effective C-hybridizations in both saturated and unsaturated C_2X rings with those in the carbocyclic parents

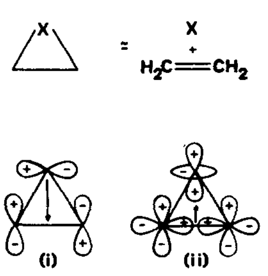

Fig. 1. Bonding model for C_2X heterocycles involving interaction between ethylene and heterogroup (X). In mechanism (i) there is donation from $X(p_x)$ (or $X(d_{xz})$) to ethylene π^*, in (ii) there is donation from ethylene π, to $X(d_{z^2})$.

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†Part IV see Ref. 8.

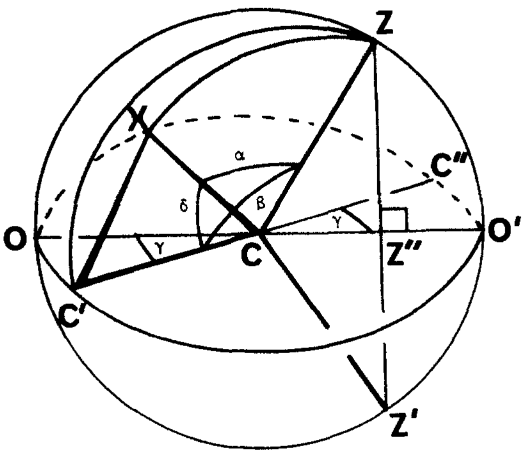
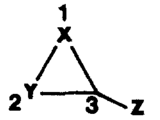


Fig. 2. Calculation of the bent-back angle (γ). In the spherical triangle construction the C_2X ring lies in the equatorial plane, while the substituent plane ZCZ' is assumed (see text) to be perpendicular to the ring. With only one substituent (Z) the bent-back angle may be calculated from the valence angles by: $\tan \gamma = (\cos \alpha / \cos \beta \sin \delta) - \cot \delta$.

Table 1. Summary of Ring Systems



	Atoms		Bond-type			Database Statistics		
Cpd	X	Y	1–2	2–3	Name(s)	N1	N2	N3
1	C	C	1	1	Cyclopropane	353	276	173
2	N	C	1	1	Aziridine (Ethyleneimine)	41	34	24
3	O	C	1	1	Oxirane	291	206	121
4	Si	C	1	1	Silirane (Silacyclopropane)	1	1	1
5	P	C	1	1	Phosphirane	1	1	1
6	S	C	1	1	Thiirane	13	12	10
7	C	C	1	2	Cyclopropene	23	17	16
8	S	C	1	2	Thiirene	4	4	4
9	N	C	2	1	1-Azirine	4	4	4
10	N	O	1	1	Oxaziridine	8	7	6
11	N	N	1	1	Diaziridine	6	4	4
12	N	N	2	1	3H-Diazirine	0	0	0

Notes. Bond-types : 1 = single, 2 = double. Database Statistics : N1 : Total no. of entries in CCD, N2 : No. of entries for which atomic coordinates are available, N3 : No. of entries (with coordinates) for which the crystallographic R-factor is less than 0.10 (0.07 in the case of compounds 1 and 3).

1 and **7**, since relative bond-strengthening or weakening is relevant to ring-opening reactions. The effect of substituents on C_2X rings is also examined. The (rather sparse) geometric data for CXY-rings is analysed in a similar manner.

METHODOLOGY

The September 1981 release of the Cambridge Crystallographic Database (CCD) has been used to obtain relevant bibliographic and numeric data for X-ray studies of organic derivatives. Substructure searches, information retrieval and data analyses were performed using computer programs described by Allen *et al.*[18] and the approaches used in earlier Parts of this series[7,8,19,20] The number of references retrieved for each ring system is indicated in Table 1, together with the number for which atomic coordinates are stored in CCD. For sparse populations relevant geometry has been taken directly from the literature in cases where coordinates were not available. Structures specifically cited in the text are referred to by CCD reference code and relevant references, ordered alphabetically by this code, are in Table 2. Gas-phase results are identified and referenced in the Standard manner. Table 1 and Fig. 2 indicate numbering schemes and designation of parameters. Error estimates for mean parameters ($\bar{x}$) are given by $\sigma(\bar{x}) = [\Sigma_n(\bar{x} - x_n)^2/n(n-1)]^{1/2}$ for n observations $x_i (i = 1, n)$. Values of $\bar{x}$ are quoted as $\bar{x}(\sigma, n)$, where n is the number of contributors to $\bar{x}$ after application of data screens based on R-factor and overall accuracy.[7,21]

SATURATED C_2X RINGS

X-ray and gas-phase geometries for saturated C_2X rings (i.e. those rings with three endocyclic single bonds) are collected in Table 3, together with data for $C(sp^3)$ substituents where available. Mean solid-state results are generated for X=C, N, O, S and show good general agreement with gas-phase data for parent rings. For X=P only one X-ray study (MPPZCH10) is available to complement the gas-phase results,[25] while the sole silirane (**4**) is the X-ray study of a bis(spirocyclopropyl) derivative (MSPSIP).

The X-ray literature contains relatively few C-*gem*-disubstituted derivatives from which to calculate the bent-back angle γ (Fig. 2); γ has therefore been calculated on a mono-substituent basis as illustrated in Fig. 2. The mean C'–C–X ring angle and mean values of the X–C–Z and C'–C–Z valence angles (α, β) are used in a spherical triangle construction. The second substituent Z' is assumed to lie below Z in a plane perpendicular to the ring, which is an approximation since the plane Z–C–Z' may twist relative to the ring plane. The approximation is close however, since for 43 oxiranes with $R \leq 0.07$ which have *gem*-di-$C(sp^3)$ substitution the mean twist angle is 88.3(3)°. For these structures precise values of γ average 20.2(4)°, which compares favourable with the 21.6° obtained via Fig. 2 after addition of mono-substituted rings. Occurrences of the substituent Z as part of a small ring (size 4 or 5) fused to C_2X have been omitted since such intra-ring angles are geometrically constrained.

sp^3-Orbital electronegativities (χ_x in eV) are quoted in Table 3, calculated using $\chi_x = a + b\delta$[27], where a is the inherent electronegativity, b is the charge coefficient and δ the partial charge on atom X. Thus χ_x will vary depending on other atoms or groups bonded to X, and are calculated from values of a_x and b_x tabulated by Huheey[27] by setting $(a + b\delta)_x = (a + b\delta)_c$ and solving using $\delta_x + \delta_c = 0$. In practice the results are very similar to Pauling's values,[28] to which scale χ_x may be converted using $\chi_x^P = 0.336(\chi_x - 0.615)$.

Electronegativity correlations

The plot of heteroatom electronegativity against C–C distance (Fig. 3a) shows an almost exact linear correlation for both X-ray and gas-phase data. The least-squares fit, based on mean X-ray geometries for X=C, N, O, S, is closely followed by the gas-phase results, including that for X=P. The X-ray result for X=P (MPPZCH10) appears to overestimate the C–C distance, while the graph suggests that C–C = 1.520(3)Å in the

Table 2. References to X-ray studies cited in this paper, ordered alphabetically by CCD reference code (see Text)

AZBNON	9,9'-Bis-9-azabicyclo(3.3.1)nonane S.F.Nelsen,W.C.Hollinsed,C.R.Kessel, J.C.Calabrese J.Am.Chem.Soc., 100, 7876, 1978
BDAZAN	N-(1,2-Di-t-butyldiaziridin-3-ylidene)-2,4,6-trimethylaniline K.Peters,H.G.von Schnering Chem.Ber., 109, 1384, 1976
BMBZDZ	bis(p-Bromo-alpha,alpha-dimethylbenzyl)diaziridinone P.E.McGann,J.T.Groves,F.D.Greene,G.M.Stack, R.J.Majeste,L.M.Trefonas J.Org.Chem., 43, 922, 1978
BONBCH	6-(p-Bromobenzoyl)-6-azabicyclo(3.1.0)hexane H.M.Zacharis,L.M.Trefonas J.Heterocycl.Chem., 5, 343, 1968
BSADAZ	N-(1'-t-Butyl-spiro(adamantane-2,2'-aziridine)-3'-ylidene)-methylamine H.Quast,P.Schafer,K.Peters, H.G.von Schnering Chem.Ber., 113, 1921, 1980
BUTSUL10	cis-2-Butene episulfone R.Desiderato,R.L.Sass Acta Crystallogr., 23, 430, 1967
DMAZOI	8,8-Dimethyl-8-azoniabicyclo(5.1.0)octane iodide L.M.Trefonas,R.Towns J.Heterocycl.Chem., 1, 19, 1965
DMTROX	2,3-Dimethylthiirene 1,1-dioxide H.L.Ammon,L.Fallon,L.A.Plastas Acta Crystallogr.,Sect.B, 32, 2171, 1976
DPTHDO	2,3-Diphenylthiirene 1,1-dioxide H.L.Ammon,L.Fallon,L.A.Plastas Acta Crystallogr.,Sect.B, 32, 2171, 1976
DPTIRO	2,3-Diphenylthiirene 1-oxide H.L.Ammon,L.Fallon,L.A.Plastas Acta Crystallogr.,Sect.B, 32, 2171, 1976
HPDIAZ	1-Cyclohexyl-3-(p-bromophenyl)diaziridine A.Nabeya,Y.Tamura,T.Kodama,Y.Iwakura J.Org.Chem., 38, 3758, 1973
IBSAZH	7-(p-Iodobenzenesulfonyl)-7-azabicyclo(4.1.0)heptane L.M.Trefonas,R.Majeste J.Heterocycl.Chem., 2, 80, 1965
IBSAZO	1-(p-Iodobenzenesulfonyl)-1-azaspiro(2.5)octane H.M.Zacharis,L.M.Trefonas J.Heterocycl.Chem., 7, 1301, 1970
INDSAZ	Spiro(indan-1,3-dione)-2,3'-(2'-phenylazirine) A.F.Mishnev,Ya.Ya.Bleidelis,L.S.Gehta Khim.Get.Soedin.,Latv.SSSR, 1217, 1977
IPAZUN	9-(p-Iodophenyl)-9-azatetracyclo(5.3.1.0(2,6).0(8,10))undec-4-ene J.N.Brown,R.L.R.Towns,L.M.Trefonas J.Heterocycl.Chem., 7, 1321, 1970
IPOXAZ	cis-2-Isopropyl-3-(p-nitrophenyl)-oxaziridine J.F.Cannon,J.Daly,J.V.Silverton,D.R.Boyd, D.M.Jerina J.Chem.Soc.,Perkin 2, 1137, 1972
MAZDCI10	cis-13,13-Dimethyl-13-azoniabicyclo(10.1.0)-tridecane iodide L.M.Trefonas,R.Towns,R.Majeste J.Heterocycl.Chem., 4, 511, 1967
MAZNOI	9,9-Dimethyl-9-azoniabicyclo(6.1.0)nonane iodide L.M.Trefonas,R.Majeste Tetrahedron, 19, 929, 1963
MAZRPZ	1,4-bis(3,3-Dimethylazirinyl)-piperazine J.Galloy,J.P.Declercq,M.van Meerssche Cryst.Struct.Commun., 9, 151, 1980
MBTAZO	bis(1,1,3,3-Tetramethylbutyl)thiadiaziridine 1,1-dioxide L.M.Trefonas,L.D.Cheung J.Am.Chem.Soc., 95, 636, 1973
MBZOCZ20	(-)-(2S)-2-((R)-alpha-Methylbenzyl)-3,3-diphenyloxaziridine A.Forni,G.Garuti,I.Moretti,G.Torre, G.D.Andreetti,G.Bocelli,P.Sgarabotto J.Chem.Soc.,Perkin 2, 401, 1978
MPPZCH10	4-Methyl-2,6,6-triphenyl-2,3-diaza-1-phosphabicyclo(3.1.0)hex-3-ene B.A.Arbuzov,V.D.Cherepinskii-Malov, E.N.Dianova,A.I.Gusev,V.A.Sharapov Dokl.Akad.Nauk SSSR, 247, 1150, 1979
MSPSIP	Dimethyldispiro(bicyclo(4.1.0)heptane-7,2'-silacyclopropane-3',7''-bicyclo(4.1.0)heptane) G.L.Delker,Y.Wang,G.D.Stucky, R.L.Lambert Junior,C.K.Haas,D.Seyferth J.Am.Chem.Soc., 98, 1779, 1976
MTBTIR10	1-Methyl-2,3-di-t-butyl-thiirenium tetrafluoroborate R.Destro,T.Pilati,M.Simonetta Nouv.J.Chim., 3, 533, 1979
MTZBCH10	trans-exo-2,4,6-Trimethyl-1,3,5-triazabicyclo(3.1.0)hexane G.B.Ansell,A.T.Nielsen,D.W.Moore, R.L.Atkins,C.D.Stanifer Acta Crystallogr.,Sect.B, 35, 1505, 1979
MXPMAZ	2,2-bis(p-Methoxyphenyl)-3-methyl-2H-azirine N.Kanehisa,N.Yasuoka,N.Kasai,K.Isomura, H.Kasai, J.Chem.Soc.,Chem.Comm., 98, 1980
OAZBCH	6-(p-Iodobenzenesulfonyl)-3-oxa-6-azabicyclo (3.1.0) hexane L.M.Trefonas,T.Sato J.Heterocycl.Chem., 3, 404, 1966
PEBPXZ10	2-(S-1-Phenylethyl)-3-(p-bromophenyl)-oxaziridine M.Bogucka-Ledochowska,A.Konitz,A.Hempel, Z.Dauter,E.Borowski Z.Kristallogr., 149, 49, 1979
PXCAZN	3-Phenoxy-3-dimethylcarbamoyldimethylamino-2-azirine J.Galloy,J.-P.Putzeys,G.Germain, J.P.Declercq,M.van Meerssche Acta Crystallogr.,Sect.B, 30, 2462, 1974
RRMBXZ	(+)-(2R)-2-((R)-alpha-Methylbenzyl)-3,3-diphenyloxaziridine A.Forni,G.Garuti,I.Moretti,G.Torre, G.D.Andreetti,G.Bocelli,P.Sgarabotto J.Chem.Soc.,Perkin 2, 401, 1978
THIRTS	2,2-Diphenyl-N-tosyl-thiiran-2-imine G.L'abbe,J.-P.Dekerk,J.P.Declercq, G.Germain,M.van Meerssche Angew.Chem.,Int.Ed.Engl., 17, 195, 1978
TSMPXZ	2-(p-Toluenesulfonyl)-3-(m-nitrophenyl)oxaziridine J.S.Chen,W.H.Watson,F.A.Davis, J.F.Lamendola Junior,U.K.Nadir Acta Crystallogr.,Sect.B, 34, 2861, 1978
TSPOXZ	2-(p-Toluenesulfonyl)-3-(p-chlorophenyl)-oxaziridine M.Kimura,W.H.Watson,F.A.Davis, J.F.Lamendola Junior,U.K.Nadir Acta Crystallogr.,Sect.B, 35, 234, 1979

Table 3. Geometric data for parent saturated C_2X-rings (distances in A, rings (distances in A, angles in degrees)

Cpd	X	C - C	C - X	C - X - C	C - C - X	C-Z (a)	X-C-Z (a)	C-C-Z (a)	Z-C-Z' (a)	γ(b)	χ(c)	Ref(d)
1	C	1.510(2,115)	1.510(2,115)	60.0	60.0	1.519(2,76)	118.3(3,76)	118.3(2,76)	114.0(4,27)	30.0	7.98	X
		1.510(2)	1.510(2)	60.0	60.0	-	117.7(Z=H)	117.7(Z=H)	115.1(Z,Z'=H)			22
2	N	1.484(3,21)	1.474(4,42)	60.5(7,21)	59.7(2,19)	1.513(2,19)	116.2(5,11)	119.1(5,11)	-	25.1	9.66	X
		1.480	1.488	60.0	60.2	-	-	-	116.7(Z,Z'=H)	20.6		10
		1.481	1.475	60.3	59.8	-	116.3(Z=H)	118.6(Z=H)	115.7(Z,Z'=H)			23
3	O	1.467(2,81)	1.447(2,162)	60.9(2,81)	59.5(2,162)	1.507(1,138)	115.2(2,159)	120.2(2,159)	115.8(3,43)	21.6	11.04	X
		1.472(2)	1.436(2)	61.4(1)	59.2(1)	-	-	-	116.6(Z,Z'=H)	20.5		11
		1.470(3)	1.434(3)	61.7(1)	59.1(1)	-	-	-	116.3(Z,Z'=H)	22.3		24
4	Si	1.520(3)	1.826(3)	49.2(1)	65.4(1)	-	138.7(e)	134.5(e)	-	35.8	7.03	X
5	P	1.519	1.879	47.7	66.2	-	114.6	117.3	117.1	31.9	8.48	X
		1.502(5)	1.867(5)	47.4(5)	66.3(5)	-	-	-	-	30.5		25
6	S	1.492(19,6)	1.820(7,12)	48.4(5,6)	65.8(4,12)	1.515(9,7)	116.9(9,7)	121.1(7,7)	-	27.1	9.17	X
		1.492(2)	1.819(2)	48.5(1)	65.8(1)	-	-	-	116.0(Z,Z'=H)	28.3		11
		1.484(6)	1.815(14)	48.3	65.9	-	-	-	115.8(Z,Z'=H)	28.2		26

Notes. (a) For X-ray studies Z = C(sp3), for gas-phase studies Z = H as indicated in the Table.
(b) Bent-back angles (γ) for X-ray work are derived from Fig. 2. Gas-phase results are taken from the reference.
(c) Electronegativity values (χ) are in eV and are calculated using data given by Huheey (ref. 27).
(d) References cited by number are individual gas-phase results; X indicates mean values obtained from the X-ray studies retrieved from CCD (note that compounds 4,5 have only one X-ray contributor).
(e) This data (from MSPSIP, Table 2) involves bis(spirocyclopropyl) substituents hence gamma is probably distorted.

silirane (MSPSIP) is somewhat shorter than might be found in the parent ring; these points are discussed more fully below.

Figure 3(b) shows a plot of the bent-back angle γ against the electronegativity, while γ is plotted against C–C distance in Fig. 3(c), following Stalick and Ibers.[17] In both cases the X-ray means for X=C, N, O, S are well correlated and have been used to derive the least-squares lines. The relationship $\Delta\gamma = 200(\Delta d_{cc})$ is given by Fig. 3(c), and the numeric coefficient is in excellent agreement with the value of 209 obtained for metallacyclopropanes.[17] The limiting value of 1.358Å for $\gamma = 0°$ is somewhat longer than the 1.333(8)Å obtained from CCD for tetra-substituted ethylenic bonds,[7] but is considerably bettter than the 1.416Å yielded by the gas-phase data.

The limited data for X=P, Si are not well fitted by Fig. 3. The occurrence of the phosphirane X-ray result virtually on the least squares line *above* X=C in Fig. 3(c) is misleading since $\chi_P > \chi_C$, and the gas-phase data for phosphirane[25] seem more realistic. For $\chi_P = 8.48$ eV Figs. 3(a, b) predict C–C=1.503Å and $\gamma = 28.7°$ for X=P. The bis(spirocyclopropyl) substituents on the C atoms of silirane in MSPSIP undoubtedly interact electronically with the C_2X ring.[14] The C_2X C–C bond is somewhat analogous to the inter-ring bond in bicyclopropyl which is formed of $\sim sp^{2.22}$ hybrids[7] and averages 1.495(5)Å for 18 accurate examples in CCD. Thus the σ-framework in the silirane of MSPSIP wil have higher C s-character than the parent ring and C–C will be foreshortened. Figs. 3a, b predict C–C = 1.526Å, $\gamma = 32.6°$ for parent silirane at $\chi_{Si} = 7.03$ eV. The predicted geometrical movements for X=P, Si are indicated in Fig. 3c.

Hybridization and C–X *bond lengths*

The hybrid orbital used by cyclopropyl C-atoms in forming bonds to substituents has been estimated from X-ray data as $\sim sp^{2.22}$ ($31\% s$) with an effective covalent radius of 0.750Å[7]. The pair of C-orbitals which contribute to the ring σ-framework in **1** then each have $\sim 19\%$ s-character ($\sim sp^{4.26}$). Table 3 shows that C–C(sp^3) substituent bond lengths decrease slightly for C_2X rings as X changes from C→N→O. The minimum value of 1.507(1)Å for X=O is a well determined mean and corresponds to $\sim sp^2$ hybridization with an effective covalent radius of 0.738Å[7]. The reality of these slight changes in exocyclic orbital hybridizations is borne out by solid state data (CCD) for the inter-ring bonds in bicyclopropyls [1.495(5,18)Å] and bioxiranyls [1.484(3,

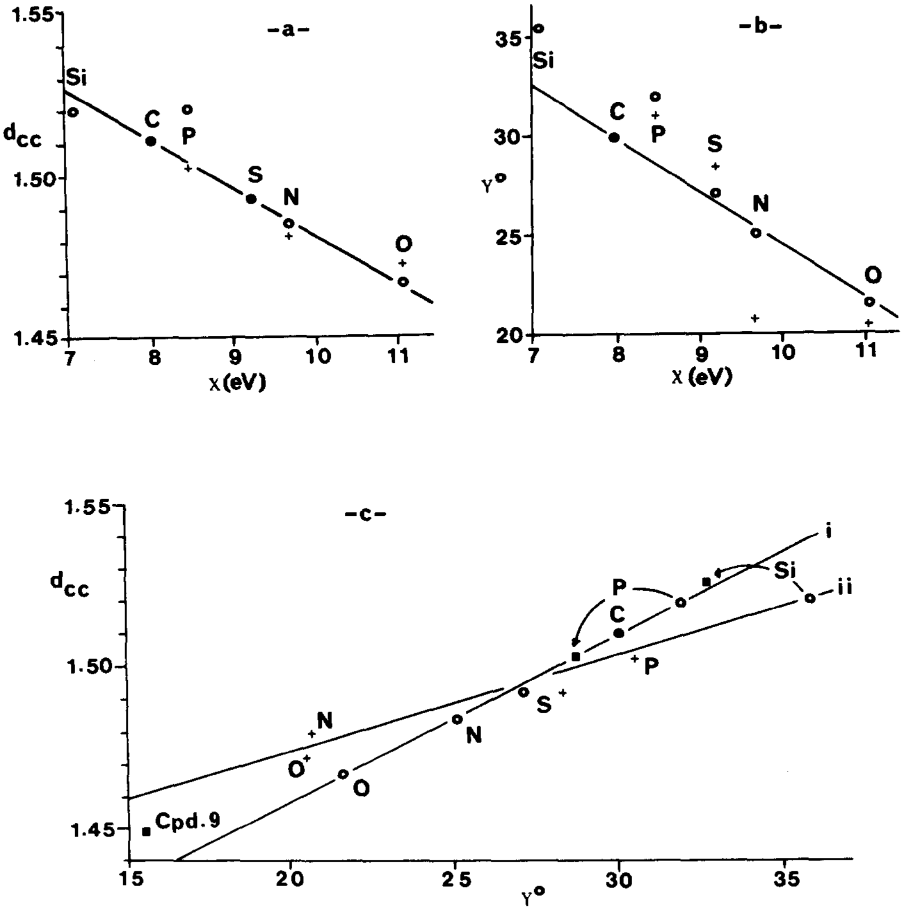


Fig. 3. (a) Plot od d_{CC} vs electronegativity (χ_X), (b) plot of γ vs χ_X, and (c) plot of d_{CC} vs γ for saturated C_2X rings, using the data of Table 3. Open circles represent X-ray data, + indicates gas-phase results. Equations of least-squares lines are: (a) $d_{CC} = 1.630 - 0.015\chi_X$; (b) $\gamma = 51.8 - 2.73\chi_X$; (c) (i, X-ray) $d_{CC} = 1.358 + 0.0050\gamma$ or $\Delta\gamma = 200\ d_{CC}$, (ii, gas-phase) $d_{CC} = 1.416 + 0.0029\ \gamma$ or $\Delta\gamma = 344\ d_{CC}$.

26)Å].[29] The corresponding exocyclic covalent radii are then 0.748Å for **1** and 0.742Å for **3**, in good agreement with values obtained above. For **2** (X=N) an exocyclic radius of 0.744 is is indicated for C, but the variety of N-substitution patterns exhibited in the X-ray literature precludes analysis of N-hybridizations.

Each C atom in a C_2X ring must therefore use some 60–66% *s*-character in forming substituent bonds, and contribute 34–40% to a pair of intra-ring σ-hybrids, depending on the electronegativity of X. We have already seen (Fig. 3a) that the C–C bond length shortens considerably as χ_x increases, or alternatively the *s*-character of the formal hybrid used in the C–C bond increases from ~19% in **1** to a maximum in **3** as χ_x increases. The angle that this hybrid makes with the C–C vector must also increase (from about 21.8° in **1**) so that the C–C shortening is accentuated by increased bending as X changes $C \to N \to O$. A similar effect obviously operates for second row X atoms. The clear implication is that the symmetrical pair of intra-ring C-hybrids in **1** become increasingly asymmetric in terms of *s*-character as χ_x increases, a conclusion supported by theoretical calculations[30–32] and by the behaviour of the C–X bond.

The C–X bonds in **1** [1.510(1)Å, Table 3] are some 0.028Å shorter than unstrained $C(sp^3)$-$C(sp^3)$ distances,[19,7] a discrepancy which is well explained theoretically.[6] Thus for X=N, O we might expect C–X to be shorter than their counterparts in unstrained systems. Table 3 shows that this is not so: C–N at 1.474(4)Å in **2** is almost equal to the unstrained 1.472(5)Å[33] while C–O in **3** at 1.447(2)Å is very significantly longer than the unstrained 1.426(5)Å[33]. Thus C–X increases significantly in length as C–C decreases, exactly as predicted above. The lengthening of C–X is almost certainly reinforced by some rehybridization at X since a comparison of ionization potentials for C_2X rings and their acyclic analogues indicates high *s*-character in the heteroatom lone pairs. For second row heteroatoms we note that C–Si in **4** [1.826(3)Å] is very much shorter than the unstrained 1.866(2)Å obtained from CCD, even allowing for the spiro substitution in MSPSIP, while C–S in **6** is almost equal to its unstrained value.[35] These differences are in line with the χ_x values since $\chi_{Si} < \chi_C$ but $\chi_S \approx \chi_N$.

An approximate empirical picture of the electronegativity-induced rehybridization at C in saturated C_2X rings may be obtained using the bent-bond approach.[2,6] Figure 4 shows that the length of the arc or bent bond (d') is geometrically related to the interorbital angle (θ) for a given C–C distance (d). Since $\cos\theta = -1/n$ for a pair of identical sp^n orbitals we can relate d' to the %*s* or %*p* character. It has also been found[7] that the single-bond covalent radius for a $C(sp^n)$ hybrid is approximated by $r = 0.408 \log p$ ($p = \%p$ character). For a C_2X C–C bond we can equate d' (as derived in Fig. 4) to $2r$ ($= 0.816 \log p$) and solve for p. Results for X = C, S, N, O are given in Table 4 and indicate an approximate distribution of available C *s*-character between C–C and C–X bonds. It should be noted that the 20.5% *s* obtained here for **1** is very close to the 19% estimated by analysis of C-substituent distances[7] and lends some credence to the approximations.

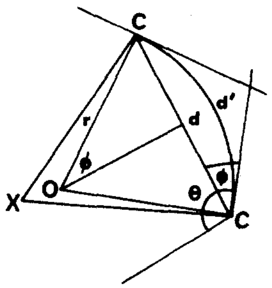


Fig. 4. Calculation of the 'arc' or 'bent' bond (d'). For an interorbital angle θ, $\phi = (\theta - v)/2$ (where v is the Z-C-C valence angle). (d') is the arc of a circle, centre O, of radius $r = d/(2, \sin\phi)$. Hence: $d' = (2\pi\phi d/360 \sin\phi)$.

Table 4 shows that the *s*-character of the C–C hybrids increases as χ_x increases and d_{cc} contracts. The angles θ and ϕ (Fig. 4) increase and the C–C bond becomes increasingly bent for the series X = C, N, O, placing the centre of bonding electron density increasingly further from the C–C internuclear vector. In the C–X bonds the C *s*-character decreases with increasing χ_x, hence θ', ϕ' and the degree of bending all decrease, moving the centre of bonding electron density closer to the internuclear line. These results are in broad general agreement with theoretical calculations[30–32] although Talaty and Simons[32] argue that the bent bond d' (Fig. 4) should remain relatively constant in length for X = C, N, O, which conflicts with data in Table 4. Nevertheless the X-ray data confirm the relative weakness of the C–X bond in **2** and **3** and it is these bonds which cleave under electrophilic or nucleophilic attack.

The model proposed above also provides explanation for the electronegativity dependence of the bent-back angle γ (Fig. 2). In **1** the methylene groups adopt a symmetrical disposition (at $\gamma = 30°$) to two symmetrical intra-ring hybrids. As the intra-ring hybrids become increasingly assymmetric in *s*-character the angle between the C–C orbital and the C-substituent orbitals increases for $\chi_x > \chi_C$, hence γ decreases from 30°.

Table 4. Empirical rehybridization model for C atoms in saturated C_2X-rings. (For definition of parameters see footnotes and Fig. 4)

		C – C Bond									Subst.	C – X Bond				
X	χ(eV)	d	v	θ	ϕ	d'	2r	%p	%s	sp(n)	%s	%s	%p	sp(n)	θ'	ϕ'
C	7.98	1.510	60.0	104.9	22.5	1.551	1.551	79.5	20.5	3.88	59.0	20.5	79.5	3.88	104.9	22.5
S	9.17	1.492	65.8	109.5	21.8	1.529	1.530	75.0	25.0	3.00	63.0	12.0	88.0	7.33	97.8	16.0
N	9.66	1.484	59.7	108.9	24.6	1.531	1.532	75.5	24.5	3.08	63.0	12.5	87.5	7.00	98.2	19.3
O	11.04	1.467	59.5	111.7	26.1	1.519	1.520	73.0	27.0	2.70	35.0	8.0	92.0	11.50	95.0	17.7

Parameters. X : heteroatom, χ : electronegativity, v : intra-annular valence angle at carbon,
θ : inter-orbital angle, ϕ : angle between bond vector and the orbital direction,
d' and 2r : length (in A) of the 'arc' or 'bent' bond derived from the equations in Figure 4,
sp(n) : estimated effective hybridization of C in the C – C or C – X bond,
Subst (%s) : total %s-character used by C in forming bonds to substituents. For X = C this is estimated from the equations of Figure 4 (see below), for X = S, N, O, it is estimated from the C – C(sp3) substituent bond lengths discussed in the text.

Substituent effects. There has been a suggestion[34] that bond lengths in fused C_2X rings increase with increasing fused-ring size. This was based on some early X-ray studies of derivatives of **2** (BONBCH, DMAZOI, IBSAZH, IBSAZO, IPAZUN, MAZDCIIO, MAZNOI, OAZBCH) and has been tested here using the more extensive oxirane data. The results of Table 5 show no upward trend in overall dimensions and no significant deviations from overall mean dimensions for **3** cited in Table 3.

There are no consistent trends discernible in the geometry of C_2X ($X \neq C$) rings having π-acceptor substituents which are comparable to those clearly observed in **1**.[19] Some 40 oxiranes with $R \leq 0.10$ are substituted by CO groups which show a wide range of conformations with respect to the ring but no obvious preferred arrangements. A number of aziridines occur in CCD with $C(sp^2)$-substitution at *N*. These are primarily carbonyl and phenyl groups, which all adopt a near perpendicular conformation[19] with respect to C_2N, but mean ring geometry does not differ significantly from values in Table 3. In X-ray studies of N-substituted arizidine (19 occurrences with $R \leq 0.10$) N is clearly pyramidal in all cases, the N-substituent bonds make a mean angle of 55.5(5)° with C_2N, and have a mean valence angle at N of 119.3(6)°.

There are no examples in CCD of an oxirane carrying π-donor substituents (e.g. halogens, =O, $=CH_2$ etc.), however spirocyclopropyloxirane has been studied by microwave methods.[35] Geometric data (Table 6) show that the C–O, C–C bonds of **3** involving the spiro C atom are shortened to 1.416(10) and 1.447(6)Å respectively, while the distal C–O bond lengthens to 1.460(4)Å. This is due to symmetrical sp^3 hybridization at the spiro C atom which increases the *s*-character of all bonds in which it is involved, hence geometric variations are directly comparable to those in spirocyclopentane[26] (Table 6). There are only three examples of a $C(sp^2)$ atom carrying an exocyclic double bond forming part of a C_2X ring. Relevant geometry for an aziridineimine (BSADAZ), a thiirane-imine (THIRTS) and a thiiranone[37] are in Table 6. The C–N, C–S bonds opposite the substituent all increase by up to 0.10Å, reminiscent of π-donor induced distal bond lengthening in cyclopropane[19] (data for cyclopropanone[38] are in Table 6 for comparison). The ring C–X and C–C bonds vicinal to the substituent both shorten, but C–C shortening (expecially in BSADAZ) is small compared to the effect on vicinal C–X. A donor effect[39,40] is clearly present here, as it is for CXY rings discussed below. The remaining 'saturated' C_2X rings having exocyclic double bonds are thiiran-1-oxide and thiiran-1,1-dioxide. Relevant gas-phase[41,42] and X-ray data are in Table 6 with parent **6** included for comparison. These compounds will be discussed below in conjunction with thiirene (**8**) and its oxides, with which they form a coherent grouping.

Table 5. Comparison of oxirane ring bond lengths (A) in fused systems for various sizes of fused ring (r)

r	C – O	C – C	N (a)	R (b)
5	1.451(3)	1.464(2)	30	0.070
6	1.444(3)	1.464(3)	70	0.070
7 – 10	1.446(4)	1.468(4)	24	0.100

Notes. (a) N = No. of contributors to the mean
(b) R = Maximum R-factor allowed for structures contributing to the mean

UNSATURATED C_2X RINGS

Geometric data for C_2X rings containing an endocyclic double bond are collected in Table 6. The carbocyclic 'parent' cyclopropene (**7**) is well known and geometric variations and hybridization in **7** and its derivatives (including the aromatic cyclopropenium ion) have been reviewed[8]; some data from Ref. 8 are included in Table 6 for comparison purposes. The hetero-analogues of **7**, oxirene and 2-azirine, are unknown even spectroscopically,[1] but four examples of the more stable X=N tautomer 1-azirine (**9**) occur in CCD (INDSAZ, MAZRPZ, MXPMAZ, PXCAZN). In all cases the ring has maximal substitution which affords some electronic stabilization similar to that suggested for cyclopropenium and cyclopropenylidene derivatives[51,52] and provides steric protection against electrophilic and nucleophilic attack. Experimental data for **9** show quite a wide range, perhaps suggestive of substituent effects, but data is sparse and an overall mean is cited in Table 6. C=N is comparable with unstrained values[53] (*cf* C–N in **2**), but C–N is considerably elongated by comparison with **2**. The C–C bond is foreshortened to 1.446(9), and it is interesting to note thaat the bent-back angle (γ, Fig. 2) at saturated C in **9** is 15.6°. These values are close to the least-squares line of the γ-d_{cc} plot of Fig. 3(c).

Thiirene (**8**) is more stable than oxirene or 2-arizirene and has a half life of some 2 secs at low pressure.[54] Recently the crystal structure of 1(S)-methyl-2,3-di-*t*-butylthiirenium tetrafluoroborate (MTBTIRIO) has been studied at −100°. This study effectively completes the series thiirene, thiirene-1-oxide (DPTIRO), thiirene-1,1-dioxide (DMTROX, DPTHDO) which parallels the analogous thiiranes noted above. All derivatives of **8** used in X-ray studies are protected[1] and stabilized[51,52] by 2,3-disubstitution with methyl or phenyl groups.

The geometry of **8** in MTBTIRIO directly comparable to that of **7** (Table 6) despite the charge on S. The C=C bond is localised and very short at 1.278(1)Å while the C–S bonds are almost identical to those in saturated thiirane; the geometry of **7** is related to that of **1** in a very similar way.[8] It appears that the electronegativity dependence of C–C bonds may also apply to unsaturated rings. The foreshortening of C=C for X=C, S (**7**, **8**) is 0.018Å, identical to the shortening of C–C between **1** and **6**. Such arguments predict a very short C=C bond (~1.25Å) in the unknown oxirene, which is close to the 1.26Å calculated by *ab initio* methods.[55] The mean C-substituent distances in the four thiirenes are 1.480(4)Å for $C(sp^3)$ substituents and 1.447(1)Å for phenyl. Comparable values for **7** are 1.476(3) and 1.445(3).[8] The C–$C(sp^3)$ distance for **8** implies a C-substituent hybrid of ~sp,[1,20] and 2,3-protons of considerable acetylenic character, almost identical to the situation in **7**.[51,8] There is some indication from the valence angles to substituents that a relationship similar to that in Fig. 3(c) may hold for C_2X rings having C=C bonds, but more data is needed to establish it clearly. The C-phenyl distances in **7** and **8** are short and imply conjugative stabilizing interactions with the ring double bond. In cyclopropenylidenes the ring double and single bonds lengthen by 0.024Å and 0.015Å respectively on 2,3-diphenyl substitution. Comparison of

Table 6. Geometry of miscellaneous saturated heterocycles C_2X, and available geometry of CXY rings (**8–12**).[a] Data for saturated rings (**1–6**), and for cyclopropene (**7**), and their derivatives are included for comparison (see text)

Cpd	Atom/Group (b)			Bond-Type			Bond Lengths (A)			Intra-annular angles (deg)			
No.	1	2	3	1-2	1-3	2-3	1-2	1-3	2-3	2-1-3	1-2-3	1-3-2	References and Notes (d)
'Pi-donor' - derivatives of 1 - 6													
2	N	C	C=N	1	1	1	1.571(-)	1.371(-)	1.482(-)	60.1(-)	53.3(-)	66.7(-)	BSADAZ
2c	N	C	C	1	1	1	1.474(3)	1.474(3)	1.484(4)	60.5(7)	59.7(6)	59.7(6)	Aziridine from Table 3
1c	C	C	C=O	1	1	1	1.575(12)	1.475(17)	1.475(17)	64.6(-)	64.6(-)	57.7(4)	Cyclopropanone, Ref 38
1c	C	C	C	1	1	1	1.510(2)	1.510(2)	1.510(2)	60.0(-)	60.0(-)	60.0(-)	Cyclopropane from Table 3
3	O	C	C(cp)	1	1	1	1.460(4)	1.416810)	1.447(6)	60.4(3)	58.3(4)	61.3(5)	Spiro-oxacyclopentane, Ref 35
3c	O	C	C	1	1	1	1.447(2)	1.447(2)	1.467(2)	60.9(2)	59.5(2)	59.5(2)	Oxirane from Table 3
1c	C	C	C	1	1	1	1.519(3)	1.469(1)	1.469(1)	58.9(-)	58.9(-)	62.2(1)	Spiro-cyclopentane, Ref 36
6	S	C	C=N	1	1	1	1.936(-)	1.704(-)	1.472(-)	47.2(-)	58.1(-)	74.7(-)	Thiiranimine, THIRTS
6	S	C	C=O	1	1	1	1.916(8)	1.726(8)	1.460(8)	46.9(7)	59.7(7)	73.4(7)	Thiiranone, Ref 37
6c	S	C	C	1	1	1	1.820(7)	1.820(7)	1.492(19)	48.4(5)	65.8(4)	65.8(4)	Thiirane from Table 3
6	S=O	C	C	1	1	1	1.822(3)	1.822(3)	1.504(3)	48.8(-)	65.6(-)	65.6(-)	Thiiran-1-oxide, Ref 41
6	SO2	C	C	1	1	1	1.731(6)	1.731(6)	1.590(11)	54.7(2)	62.7(-)	62.7(-)	Thiiran-1,1-dioxide, Ref 42
6	SO2	C	C	1	1	1	1.720(10)	1.743(20)	1.588(20)	54.6(8)	63.4(9)	62.0(8)	Thiiran-1,1-dioxide, BUTSUL10
Thiirenes (8)													
8	S	C	C	1	1	2	1.818(1)	1.819(1)	1.278(1)	41.1(1)	69.5(1)	69.4(1)	MTBTIR10
8	S=O	C	C(Ph)2	1	1	2	1.784(4)	1.784(4)	1.305(5)	42.9(2)	68.5(2)	68.6(2)	DPTIRO
8	SO2	C	C(Me)2	1	1	2	1.687(4)	1.687(4)	1.339(5)	46.8(2)	66.6(2)	66.6(2)	DMTROX (2 molecules)
8	SO2	C	C(Ph)2	1	1	2	1.703(3)	1.716(2)	1.353(4)	46.6(1)	67.2(2)	66.2(2)	DPTHDO
7c	C	C	C	1	1	2	1.509(1)	1.509(1)	1.296(1)	50.8(1)	64.6(-)	64.6(-)	Cyclopropene, Ref 43
7c	C=C	C	C(Me)2	1	1	2	1.391(1)	1.391(1)	1.323(4)	56.8(1)	56.8(1)	61.6(1)	Cyclopropenylidenes, means from Ref 8
7c	C=C	C	C(Ph)2	1	1	2	1.406(3)	1.406(3)	1.347(2)	57.5(2)	61.4(1)	61.4(1)	Cyclopropenylidenes, means from Ref 8
1-Azirines (9) (INDSAZ, MAZRPZ, MXPMAZ, PXCAZN)													
9	N	C	C	2	1	1	1.268(7)	1.560(20)	1.446(9)	60.4(5)	69.8(9)	49.8(7)	Mean of X-ray results
7c	C	C	C	2	1	1	1.296(1)	1.509(1)	1.509(1)	64.6(-)	64.6(-)	50.8(1)	Cyclopropene, Ref 43

Oxaziridines (10) (C-monophenyls : IPOXAZ, PEBPXZ10, TSMPXZ, TSPOXZ; C-diphenyls : MBZOCZ20, RRMBXZ)												
10	N	O	C(Ph)	1	1	1	1.496(4)	1.437(7)	1.411(3)	57.4(2)	59.2(2)	63.4(2)	Mono-phenyl derivs, mean X-ray result
10	N	O	C(Ph)2	1	1	1	1.531(10)	1.468(4)	1.427(6)	56.7(2)	59.4(4)	63.9(4)	Di-phenyl derivs, mean X-ray result
10	N	O	C	1	1	1	1.508(8)	1.447(8)	1.416(6)	57.2(2)	59.2(2)	63.6(2)	All rings
Diaziridines (11) (comparison data for C=O, C=N, SO2 derivatives are in Part 1 of this Table)													
11	N	N	C	1	1	1	1.444(13)	1.489(9)	1.489(9)	61.0(-)	61.0(-)	58.0(8)	trans lone pairs, ref 45
11	N	N	C	1	1	1	1.453(8)	1.437(9)	1.430(8)	59.3(4)	59.8(4)	60.9(4)	trans, HPDIAZ
11	N	N	C	1	1	1	1.511(6)	1.463(7)	1.443(7)	59.3(3)	58.1(3)	62.6(4)	cis, MTZBCH10
11	N	N	C=N	1	1	1	1.581(9)	1.381(9)	1.381(10)	55.1(7)	55.1(7)	69.8(7)	trans, BDAZAN
11	N	N	C=O	1	1	1	1.607(-)	1.325(-)	1.325(-)	52.7(-)	52.7(-)	74.7(-)	trans, BMBZDZ
11c	N	N	SO2	1	1	1	1.67(-)	1.62(-)	1.62(-)	59(-)	59(-)	62(-)	trans, MBTAZO
3H-Diazirines (12)													
12	N	N	C	2	1	1	1.233(3)	1.484(3)	1.484(3)	65.5(-)	65.5(-)	49.0(-)	Refs 46-48, see footnote (e)
12	N	N	C(F)2	2	1	1	1.293(4)	1.426(4)	1.426(4)	63.0(-)	63.0(-)	54.0(-)	perfluoro-3H-diazirine, ref 49
7c	C	C	C	2	1	1	1.296(1)	1.509(1)	1.509(1)	64.6(-)	64.6(-)	50.8(-)	cyclopropene, ref 43
7c	C	C	C(F)2	2	1	1	1.321(1)	1.438(7)	1.438(7)	62.7(-)	62.7(-)	54.6(7)	difluoro-cyclopropene, ref 50

Footnotes. (a) Compound numbers refer to the parent ring of Table 1. The atom numbering refers to the diagram in Table 1.

(b) The first-named atom of a group is a member of the three-membered ring. C(cp) indicates a spiro-cyclopropane ring, SO2 is sulphonyl, all other groups (Ph, Me, F) represent single-bonded substituents at the ring carbon atom.

(c) Data for this ring is included in the Table for comparison purposes (see text).

(d) X-ray work is cited by CCD reference code (Table 2), gas-phase studies are cited by numeric references.

(e) Mean gas-phase geometry from studies of parent 12 (ref. 46), and its methyl (ref. 47) and dimethyl (ref 48) derivatives.

DMTROX and DPHTDO (Table 6) shows comparable figures of 0.014 and 0.023Å for the 1,1-dioxide of **8**.

The irregular but very significant variations between the geometry of thiirane (**6**) and its oxides have been extensively studied by theoretical methods.[12,13] The C–C bond in **6** increases from 1.492(19) to 1.504(3) in the 1-oxide and to a very long 1.590(11)Å in the dioxide; C–S distances in **6** and its 1-oxide are identical but are ~ 0.09Å shorter in the dioxide. The relationship between **6** and its dioxide is reminiscent of that between **1** and cyclopropanone[38,19] (Table 6). The theoretical models[12,13] explain these phenomena in terms of S 3*d*-orbital participation and variations in donor-acceptor strengths of X = S, SO, SO_2. Similar variations occur in the thiirene series, and Table 6 might imply that the C=C lengthening is more regular (1.278, 1.305, 1.339/1.353Å) as S is progressively substituted by O. However DPTIRO is a 2,3-diphenyl derivative (see above), hence the parent 1-oxide probably has a shorter C=C bond (~1.290–1.295), while the 1.339 in DMTROX is a likely limiting value for the dioxide and is very similar to that observed[8] in the calicenes (Table 6). The C=C sequence now parallels the C–C sequence in the thiiranes in terms of irregularity. It should be noted, however, that the baseline (MTBTIRIO) for **8** is ionic, and that C–S distances for the thiirene series *do* seem to decrease regularly on oxygen addition. It would appear that more experimental data in these interesting systems are desirable. Nevertheless the effect of X=SO_2 on C–C and C=C bonds is dramatic, as it is in the thiadiaziridine MPTAZO (Table 6) where N–N is elongated to 1.67Å!, and the effect may have synthetic utility since such long bonds must be very weak.

CXY-RINGS

X-ray and gas phase data for oxaziridines (**10**), diaziridines (**11**) and 3H-diazirines (**12**) are collected in Table 6. Although data is sparse, some comparisons may be drawn with the preceding analysis of C_2X rings and the unstrained systems.

Oxaziridine (10)

Six accurate ($R \leq 0.10$) examples of **10** occur in CCD, all are stabilised and protected by bulky substituents at N, while four (IPOXAZ, PEBPXZIO, TSMPXZ, TSPOXZ) have C-monophenyl substitution and two (MBZOCZIO, RRMBXZ) are C-diphenyl derivatives, Mean CNO-ring geometry is listed in Table 6 for mono- and diphenyl derivatives and for all six rings. The phenyl rings may have some effect on ring geometry, but do not adopt a preferred conformation with respect to the ring. However, the overall mean C-phenyl distance (1.494(6)Å) and Ph–C–Ph angle of 117.9(6)° imply that the C-substituent hybrids approach sp^2. The overall mean for the ring shows an N–O bond some 0.05Å longer than in unstrained systems (as determined from CCD): the relative weakness of heteroatom-heteroatom bonds in CXY rings has been deduced from simple heat-of-formation calculations.[1] The C–O, C–N bonds are progressively shorter than their unstrained analogues, by 0.01 for C–O and 0.025Å for C–N. The C–N bond is therefore the strongest, in line with the relative stability of oxaziridines and their nitrone isomers.[56]

Diaziridine (11)

Parent **11** has been studied by electron diffraction. The lone pairs on N are *trans* (i.e. the torsion angle, ϕ, between lone pairs about the N–N bond is ~130°) and the N–N bond is a little shorter than the value in hydrazines.[33] The only X-ray study (HPDIAZ) of a derivative of **11** with *trans* lone pairs has N–N = 1.453(8)Å very close to the hydrazine value of 1.451(5)Å.[33] There is, however an inexplicable difference in C–N distances between the gas-phase result and HPDIAZ. The X-ray result shows short, strong C–N bonds, with N–N almost identical to unstrained values and hence weak, in agreement with thermochemical data.[1] In MTZBCHIO the N lone pairs are held in the *cis* position ($\phi = 0°$) by ring fusion at N–N, and the bond length is 1.511(6)Å. This is in agreement with the N–N torsional potential curve,[57] where lone-pair lone-pair repulsion is maximized at $\phi = 0$ and $\phi = 180°$. The N–N distance in MTZBCHIO is comparable to an unstrained value of 1.505(3)Å observed in AZBNON (where ϕ is sterically constrained at 180°) and must be relatively weak as expected.[1]

The effect of exocyclic double bonds at C on the N–N distance in **11** is comparable to their effect on distal bonds in cyclopropane[19] (see Table 6). The N–N bond length increases dramatically, while C–N contract to very short values. The X-ray studies of BDAZAN, BMBZDZ (and MBTAZO) all have *trans* ($\phi \sim 130°$) lone pairs, and the N atoms are clearly pyramidal. The effect of X=SO_2 (MBTAZO) has been noted above, and the presence of exocyclic double bonds suggests that ring opening by N–N cleavage is extremely facile.[58]

3H-*Diazirine* (12)

3H-diazirine is more stable than diazomethane[60] and has been studied in the gas phase. The data in Table 6 is an average of results for **12**[46] and its monomethyl[47] and dimethyl[48] derivatives. The N=N bond is short, while C–N distances are comparable with values in **11**.[45] This behaviour resembles that of cyclopropane[43] (Table 6) and it is not surprising that π-donor difluoro-substitution at C in **12** has an almost identical geometric effect on **12**[49] and **7**.[50] Thus the N=N distance increases significantly and C–N contract by some 0.06Å; the hybridization changes underlying these geometric variations have already been discussed.[8]

SUMMARY AND CONCLUSIONS

This paper tabulates and reviews the geometry of C_2X and CXY heterocycles as determined by X-ray and gas-phase methods. The geometric parameters of heterocycles are compared with each other, and with the 'parent' carbocycles cyclopropane (**1**) and cyclopropene (**7**). The following conclusions are obtained:

(i) In saturated C_2X rings the C–C bond length (d_{cc}) and bent back angle (γ in Fig. 2) decrease linearly with increasing hetero-atom electronegativity (χ_x). Relationships are established between χ_x and d_{cc}, χ_x and γ, d_{cc} and γ, from mean solid-state geometries for X=C, N, O, S, which enable predictions to be made for X=Si P. These effects are explicable in terms of interaction of the heteroatom with ethylene[12–14] and are analogous to the formation of metallacyclopropanes.[15–17] The C–X bond length shows an effective increase as χ_x increases, in line with facile ring-opening involving C–X bonds.[1]

(ii) A simple model for hybridization changes at C in saturated C_2X rings is derived empirically using the bent-bond approach.[2,6] The results are in broad agreement with theoretical calculations.[30–32]

(iii) There is no evidence for geometric variations in C_2X rings induced by π-acceptor substituents; such effects *are* observed for **1**.[19] π-Donor substituents do appear to interact electronically with heterocyclic rings to produce distal bond lengthening and vicinal shortening.[19,8]

(iv) Quantitative geometric variations in unsaturated C_2X and CXY rings are directly comparable to those in **7** and its derivatives.[8] It appears that C–C double bonds in C_2X systems also vary with χ_x in a systematic manner.

(v) Heteroatom-heteroatom bonds in CXY rings are weak, N–O in **10** is weaker than N–N in **11**, in agreement with thermochemical data.[1] These bonds are further weakened by distal π-donor substitution.

It has been the purpose of this series[7,8,19,20] to show that small variations in the electronic distribution in molecules leave their trace in the molecular geometry determined in the solid state. Frequently such small variations are not conclusively established by an individual X-ray study: the results of many studies of a fragment, in chemically identical or similar environments, must be carefully averaged. It is then that variations which are of marginal significance in an individual analysis either contribute to a significant trend, or, perhaps, stand out from the average. The C–C bond in BUTSUL10 and the N–N bonds in BDAZAN and MBTAZO (Table 6) are gross examples of such outliers, while some of the very small π-acceptor substituent effects in cyclopropane (0.014–0.026Å),[19] or even the difference between C–C bond lengths in oxirane and aziridine (0.017Å, Table 3), reveal detail at a much finer level.

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