Captodative Substitution and Cyclopropane Geometry. Part 5.[1] X-Ray Structure of Five New Compounds and Asymmetry Parameters of the Substituents

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Five new captodative (cd) substituted cyclopropanes have been synthesized and their structures determined from *X*-ray diffraction data. These are *cis*-1,2-dicyano-1,2-dimethyl- (**1**), *trans*-1,2-dicyano-1,2-bisethoxycarbonyl- (**2**), *cis*-1,2-dicyano-1,2-dimethoxy- (**3**), *trans*-1,2-dicyano-1,2-bismethylthio- (**4**), and *trans*-1,2-dicyano-1,2-bis(dimethylamino)-cyclopropane (**5**). These structures have been solved by direct methods and refined by least-squares using 865, 1 332, 766, 1 075, and 1 341 reflections respectively, to *R* 0.062, 0.041, 0.044, 0.031, and 0.049. This work completes former results and permits the discussion of the influence of polar substituents on cyclopropane geometry in relation to their reported ease of *cis–trans* isomerization. The effect on ring bond lengths is small but significant: in both captodative and dicapto-substitution, the distal ring bond is shortened and vicinal bonds are lengthened. Mean distal-bond shortenings are proposed for SR, OR, and NR_2; the values calculated for C≡N, C=O, and phenyl agree with published data. The particular facile isomerization of cd cyclopropanes appears best explained, not as the consequence of a destabilized ground state but rather as increased spin delocalization in the transition state.

Substituent-induced bond-length variations in cyclopropane derivatives have been studied because they afford information about the ability of cyclopropane to conjugate with adjacent substituents. From the collection of all geometrical data up to 1981, Allen[2] has shown that π-acceptor substituents shorten the distal ring bond and lengthen the vicinal bonds. Since for donor and for *gem* or vicinal donor–acceptor substituents, data are sparse and conclusions are less clear we undertook our work. In previous papers,[1,3–5] we have reported the *X*-ray structures of six captodative (cd)† and also dicapto (cc) substituted derivatives. The geometries of these new cyclopropane derivatives have been correlated with the very low energies of *cis–trans* isomerization of cyclopropanes[7] with cd-substitution.

In a further effort to quantify the effect of substituents on cyclopropyl geometry we have now established the *X*-ray structures of further five new cd or cc substituted cyclopropanes. We report here the crystal structures of compounds (**1**)—(**5**). The results together with those of formerly studied cd-substituted cyclopropanes,[1,3–5] a total of 11 molecules, permit insight into substituent-induced bond-length asymmetry parameters. Our new *X*-ray structures also permit comparison with our kinetic studies of *cis–trans* isomerizations of cd-substituted cyclopropanes.[7]

	R^1	R^2	R^3
(**1**)	CH_3	CN	CH_3
(**2**)	COOEt	COOEt	CN
(**3**)	OCH_3	CN	OCH_3
(**4**)	SCH_3	SCH_3	CN
(**5**)	NMe_2	NMe_2	CN

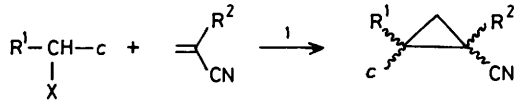
Synthesis of Cyclopropanes (**1**)—(**12**).—Only the broad approach to the new cyclopropanes (**2**)—(**12**) is reported here; details will be given elsewhere. The already known 1,2-dicyano-1,2-dimethylcyclopropane (**1**) was prepared as described.[8] For the synthesis of compounds (**2**)—(**12**), two approaches were followed. In the first, the three-membered ring is constructed by carbenoid addition to olefins (Schemes 1 and 2). In the second, either 1,3-dianions are cyclized by oxidation

† Captodative (cd) substitution means the simultaneous substitution on the same carbon atom by an electron acceptor group (c) (*i.e.* CN, COOR) and an electron donor group (d) (*i.e.* OR, SR, NR_2).[6]

Table 1.

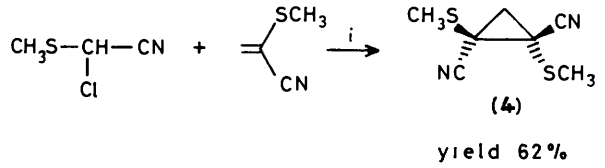
Product	Yield (%)	*cis*:*trans* (%)
(**2**)	40	only *trans*
(**6**)	74	61:39
(**7**)	85	63:37
(**8**)	88	55:45
(**9**)[a]	73	75:25
(**10**)	62	87:13

[a] NaH was used as base as for other cd-cyclopropane syntheses.[9] Since, however, derivative (**4**) is not accessible by this method (known as the McCoy reaction[10]), in this case, copper isonitrile complexes[11] were used but only the *trans* isomer (**4**) can be isolated after chromatography (Scheme 2).



(**2**) X = Br, c = CN, R^1 = R^2 = COOEt
(**6**) X = Br, c = CN, R^1 = COOMe, R^2 = SBu^t
(**7**) X = Cl, c = CN, R^1 = SPh, R^2 = SBu^t
(**8**) X = Cl, c = CN, R^1 = Ph, R^2 = SBu^t
(**9**) X = Cl, c = COOMe, R^1 = Cl, R^2 = SBu^t
(**10**) X = Cl, c = CN, R^1 = SPh, R^2 = SMe
c = captor group

Scheme 1. *Reagents:* i, Bu^tOK or NaH, THF, 20 °C, 12 h

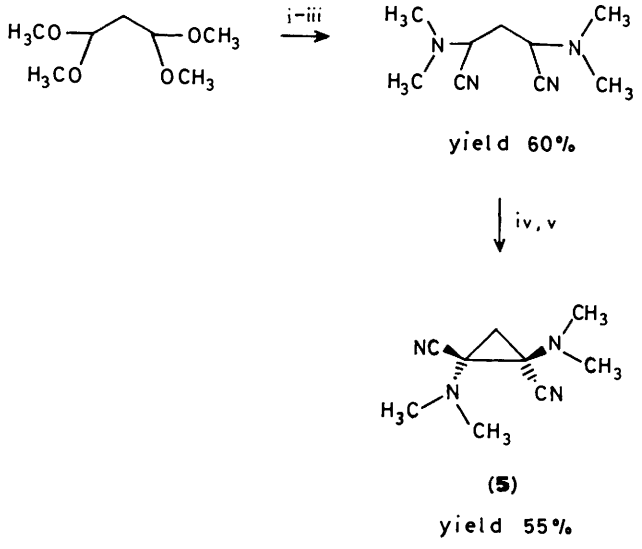


Scheme 2. *Reagents:* i, Bu^{t}N=C, Cu_2O, PhH, reflux, 6 h

(Schemes 3 and 5) or by reduction of the corresponding 1,3-dibromepropane derivatives (Scheme 4).

Table 1 summarizes the results according to Scheme 1 with *cis–trans* ratios and with the yields of compounds (**2**) and (**6**)—(**10**) obtained by addition of carbanions bearing a leaving group α to olefinic Michael acceptors (Scheme 1).

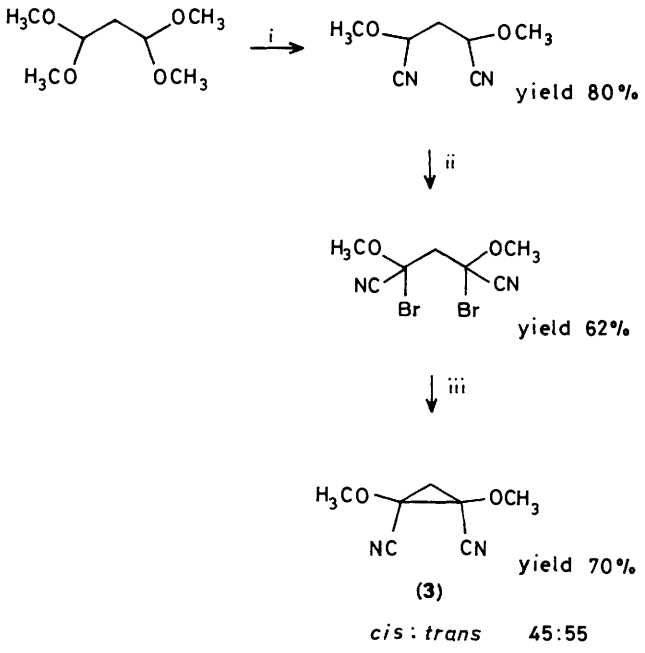
Three factors restrict this approach, the instability of some carbanionic precursors or of their olefinic partners, their ease of dimerization such as in the case of α-methylthioacrylonitrile,[12] and finally the reluctance of α-cyanoenamines and α-cyano enol ethers to act as Michael acceptors. Thus the second approach *via* 1,3-dianion oxidation was developed. The corresponding 1,3-bis-cd-substituted propanes were obtained either by the Strecker reaction of malondialdehyde (Scheme 3), or by treatment of 1,3-tetramethoxypropane with trimethylsilyl cyanide[13] (Scheme 4), and also by substitution of di-iodomethane (Scheme 5).



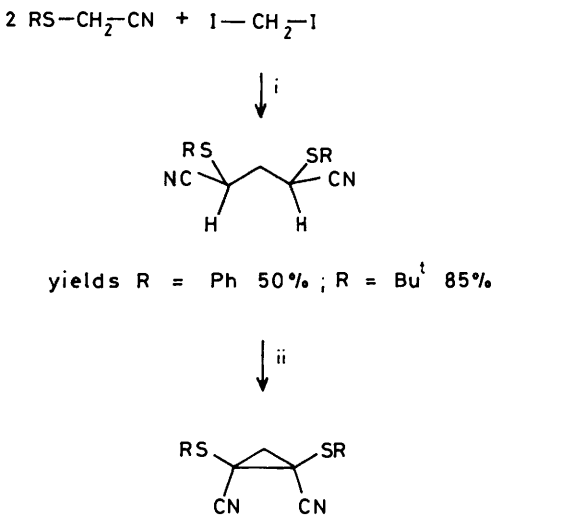
Scheme 3. *Reagents:* i, HCl 1N, 0 °C, 24 h; ii, aqueous $NaHCO_3$ (neutralization); iii, Me_2NH_2Cl, NaCN, H_2O, 0—20 °C, 3 h; iv, 2 equiv. Bu^{t}Li, THF, −78 °C, 1 h; v, 1 equiv., I_2, THF, −78 °C, 3 h

Cyclopropanes (**5**), (**11**), and (**12**) were synthesized from corresponding open chains by treatment with two equivalents of base at low temperature followed by one equivalent of iodine (Schemes 3 and 5). The cyclization mechanism is uncertain; it may proceed *via* an S_Ni type substitution of the monoiodo intermediate or *via* coupling of the 1,3-radical anion or diradical formed by oxidation of the corresponding 1,3-dianion.[14] Owing to the captodative substitution,[6] either radical pathway appears favoured.[15]

Compound (**3**) was obtained after 1,3-dibromination of the open-chain compound followed by reductive cyclization with activated zinc powder (Scheme 4). In cases where *cis*:*trans* mixtures were obtained, these were separated by flash chromatography on silica gel, then recrystallized from ether–light petroleum. It is important to note that *cis–trans* isomerization of some of those cd-substituted cyclopropanes



Scheme 4. *Reagents:* i, 0.1 equiv. $SnCl_2$, 2 equiv. Me_3SiCN, 20 °C, 1 h; ii, 2 equiv. NBS, $(PhCO_2)_2$ (5%), CCl_4, reflux, 2 h; iii, Zn, acetone, 3 h, 20 °C



Scheme 5. *Reagents:* i, NaH, DMF, 20 °C, 12 h; ii, 2LDA, TMEDA, I_2

occurs at room temperature, the equilibrium favouring the more stable *trans* isomer.[7]

Crystal Data.—Crystallographic data are presented in Table 2. The unit-cell parameters and their standard deviations were obtained by a least-squares best fit to the setting angles of 15 [25 in the case of (**5**)] reflections in the range $5 \leqslant 2\theta \leqslant 35°$. Single-crystal *X*-ray diffraction data were collected with a Syntex $P2_1$ or a Huber four-circle diffractometer using ω scan mode and radiation as described in Table 2. In each case, a standard reflection was checked every 50 reflections and no significant deviation was observed. Lorentz and polarization corrections were applied but no absorption corrections were made.

The five structures were solved by direct methods with the

Table 2. Crystal data, data collection, and results of refinements

Compound	(1)	(2)	(3)	(4)	(5)
Formula	$C_7H_8N_2$	$C_{11}H_{12}N_2O_4$	$C_7H_8N_2O_2$	$C_7H_8N_2S_2$	$C_9H_{14}N_4$
M	120.15	236.23	152.15	184.28	178.24
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a (Å)	15.201(5)	11.924(2)	8.453(3)	10.223(4)	7.008(1)
b	6.882(2)	9.918(3)	15.850(7)	12.336(5)	9.851(2)
c	6.845(2)	11.712(2)	6.781(2)	7.411(3)	15.644(4)
β (°)	93.39(2)	119.53(2)	112.77(3)	91.69(3)	101.59(2)
U (Å^3)	714.8(4)	1 205.2(5)	837.7(6)	934.2(6)	1 058.0(3)
Z	4	4	4	4	4
D_x (g cm^{-3})	1.12	1.08	1.21	1.31	1.12
F(000)	256	496	320	384	384
Diffractometer	Syntex $P2_1$	Syntex $P2_1$	Syntex $P2_1$	Syntex $P2_1$	Huber 4 circles
X-Ray radiation [λ (Å)] graphite-monochromatized Ni-filtered	Cu-K_α(1.5418) *	Mo-K_α(0.710 69) *	Mo-K_α(0.710 69) *	Mo-K_α(0.710 69) *	Mo-K_α(0.710 69) *
Crystal dimensions (mm^3)	0.3 × 0.35 × 0.25	0.2 × 0.2 × 0.2	0.4 × 0.25 × 0.25	0.42 × 0.4 × 0.05	0.3 × 0.3 × 0.4
μ (cm^{-1})	5.55	1.08	0.98	4.93	0.78
2θ range	3—114	3—47	3—47	3—47	3—50
No. of reflections measured	908	1 784	1 244	1 376	1 756
No. of reflections with $I > 2.5\sigma(I)$ used in structure refinement	865	1 332	766	1 075	1 341
No. of observed H	all	9	all	all	all
No. of calculated H	—	3	—	—	—
S	0.61	0.95	1.42	0.62	2.04
Max and min heights in final difference Fourier (e Å^{-3})	0.15—0.31	0.17—0.20	0.12—0.26	0.20—0.17	0.18—0.22
Max shifts/error	0.09	0.11	0.89	0.04	0.02
$R(= \Sigma\Delta/\Sigma F_o)$	0.062	0.041	0.044	0.031	0.049
R_w	0.070	0.049	0.044	0.031	0.054
Weight $w = 1/(\sigma^2 + gF^2)$	g = 0.0304	0.0035	0.0004	w = 1	0.0008

Table 3. Atomic co-ordinates (× 10^4) of *cis*-1,2-dicyano-1,2-dimethylcyclopropane (**1**)

	x	y	z
C(1)	907(1)	2 000(2)	8 166(2)
C(2)	1 832(1)	1 959(2)	7 434(2)
C(3)	1 197(1)	321(3)	7 000(2)
C(4)	843(1)	1 670(2)	10 254(2)
C(5)	230(1)	3 424(3)	7 307(3)
C(6)	2 090(2)	3 350(4)	5 867(3)
C(7)	2 543(1)	1 561(3)	8 894(3)
N(1)	782(1)	1 410(3)	11 881(2)
N(2)	3 113(1)	1 278(3)	10 009(3)

Table 4. Atomic co-ordinates (× 10^4) of *trans*-1,2-dicyano-1,2-bisethoxycarbonylcyclopropane (**2**)

	x	y	z
C(1)	9 155(2)	7 187(2)	4 055(2)
C(2)	9 587(2)	8 412(2)	3 517(2)
C(3)	9 472(3)	7 014(3)	2 965(2)
C(4)	10 043(2)	6 691(2)	5 361(2)
N(5)	10 701(2)	6 248(2)	6 370(2)
C(6)	7 755(3)	7 122(3)	3 656(2)
O(7)	6 914(2)	7 345(2)	2 552(2)
O(8)	7 574(2)	6 799(2)	4 641(2)
C(9)	6 235(3)	6 622(4)	4 340(3)
C(10)	5 780(4)	5 251(5)	3 832(4)
C(11)	8 623(3)	9 415(3)	2 772(2)
N(12)	7 908(3)	10 248(2)	2 189(3)
C(13)	10 898(2)	9 025(2)	4 339(2)
O(14)	11 063(2)	10 219(2)	4 481(2)
O(15)	11 799(2)	8 094(2)	4 855(2)
C(16)	13 126(3)	8 549(4)	5 614(4)
C(17)	13 693(3)	8 674(5)	4 746(5)

MULTAN 80[16] or SHELX 86[17] [for (**4**)] programs. They were all refined by full-matrix least-squares analysis first with isotropic and then anisotropic temperature factors using SHELX 76.[18] At this stage, all [but three of a methyl group of compound (**2**)] hydrogen atoms were located from Fourier difference synthesis. The positions of these atoms were then included in three further refinement cycles with common isotropic temperature factors. The three hydrogen atoms of the methyl group on C(17) of (**2**) were calculated at C–H distances of 1.08 Å. For compound (**4**), a Fourier difference synthesis revealed two positions (A and B) for the microcycle. These two positions were perpendicular to each other with distinct C(1) and C(2) but common C(3) positions; C(1B) and C(2B) were included in the three last refinement cycles with isotropic temperature factors. The refined occupation factors were 0.84 for position A and 0.16 for position B. Final R and R_w values are given in Table 2. Atomic co-ordinates for the five compounds are presented in Tables 3—7.

Discussion

Interatomic distances and bond angles are deposited in the Cambridge Crystallographic Data Centre. Views of molecules (**1**)—(**5**) with atom numbering are presented in Figures 1—5.[19]

Geometrical Features.—Apart from the cyclopropyl ring distances discussed later, detailed inspection of the geometries of the five molecules (**1**)—(**5**) reveals some interesting features. The mean interatomic distances C–CN and C≡N are 1.456(3) and 1.137(3) Å. These values are slightly but significantly different from those reported for 14 cyanocyclopropanes, C–C≡N = 1.441(4), C≡N = 1.143(3) Å.[12] The distances C_{ring}—CO_2Me [mean value 1.499(2) Å] and C=O (mean 1.200(2) Å) in

Table 5. Atomic co-ordinates ($\times 10^4$) of *cis*-1,2-dicyano-1,2-dimethoxycyclopropane (**3**)

	x	*y*	*z*
C(1)	5 089(4)	3 159(2)	3 946(4)
C(2)	6 644(4)	3 683(2)	4 024(5)
C(3)	6 346(5)	2 810(2)	3 128(6)
C(4)	5 073(4)	2 860(2)	5 962(6)
C(5)	2 700(6)	4 057(3)	3 081(8)
C(6)	7 400(8)	4 529(4)	1 676(10)
C(7)	8 048(5)	3 817(2)	6 105(6)
N(1)	5 017(4)	2 640(2)	7 536(5)
N(2)	9 147(4)	3 935(2)	7 708(6)
O(1)	3 520(3)	3 379(2)	2 436(3)
O(2)	6 255(3)	4 379(2)	2 719(4)

Table 6. Atomic co-ordinates ($\times 10^4$) of *trans*-1,2-dicyano-1,2-bismethylthiocyclopropane (**4**)

	x	*y*	*z*
C(1A)	3 375(3)	1 666(3)	1 020(4)
C(2A)	4 673(4)	2 269(3)	665(5)
C(3)	3 916(3)	1 713(3)	−837(4)
C(4)	2 260(3)	2 370(3)	1 376(4)
C(5)	5 854(3)	1 711(3)	1 364(4)
C(6)	3 466(4)	803(3)	4 449(5)
C(7)	4 952(5)	4 016(4)	2 960(6)
N(1)	1 329(3)	2 792(3)	1 699(4)
N(2)	6 833(3)	1 404(3)	1 879(4)
S(1)	3 414(1)	376(1)	2 126(1)
S(2)	4 690(1)	3 711(1)	609(1)
C(1B)	3 680(18)	2 523(14)	624(21)
C(2B)	4 344(18)	1 415(14)	1 105(22)

Table 7. Atomic co-ordinates ($\times 10^4$) of *trans*-1,2-dicyano-1,2-bis(dimethylamino)cyclopropane (**5**)

	x	*y*	*z*
C(1)	4 316(3)	2 674(2)	3 054(1)
C(2)	6 216(3)	2 926(2)	3 716(1)
C(3)	6 250(4)	2 498(3)	2 798(2)
C(4)	3 285(4)	1 434(3)	3 200(2)
N(5)	2 353(4)	514(3)	3 287(2)
N(6)	3 149(3)	3 816(2)	2 724(1)
C(7)	2 139(6)	3 597(4)	1 827(2)
C(8)	1 817(4)	4 211(3)	3 291(2)
C(9)	6 669(4)	4 344(3)	3 938(2)
N(10)	7 135(4)	5 407(3)	4 180(2)
N(11)	6 757(3)	1 944(2)	4 388(1)
C(12)	5 789(6)	2 171(4)	5 123(2)
C(13)	8 857(5)	1 830(4)	4 668(2)

(**2**) are similar to the means of 1.484(4) and 1.209(3) Å calculated for carbonyl-substituted cyclopropanes.[20] Nevertheless these values correspond much more to unconjugated carbonyl groups for which the means are 1.504(6) and 1.203(5) Å; this does not agree with the observed bisecting conformations of these substituents in (**2**). Indeed the torsion angles, τ, O(7)–C(6)–C(1)–*M*23 = 11° and O(14)–C(13)–C(2)–*M*13 = −167° with *M*13 and *M*23 the midpoints of the bonds C(1)–C(3) and C(2)–C(3) are clearly values of bisecting conformations. The bond lengths C_{ring}–OMe, mean 1.371(3) Å in (**3**), C_{ring}–SMe, mean 1.796(3) Å in (**4**), and C_{ring}–NMe_2, mean 1.424(2) Å in (**5**) are in agreement with reported values.[1,3–5,21,22,23] The bond angles around the cyclopropane carbons, except the endocyclic angles, varied from 112.0(2) to 121.8(1)°. For compounds (**1**), (**4**), and (**5**) the angles X–C_{ring}–C_{ring} with X = Me (**1**), SMe (**4**), or NMe_2 (**5**) are opened. For compounds (**2**) and (**3**) the values

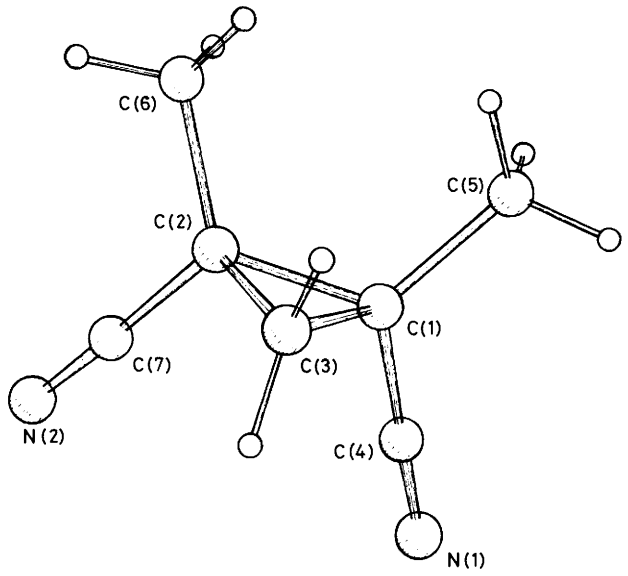


Figure 1. View of compound (**1**) and atom numbering[19]

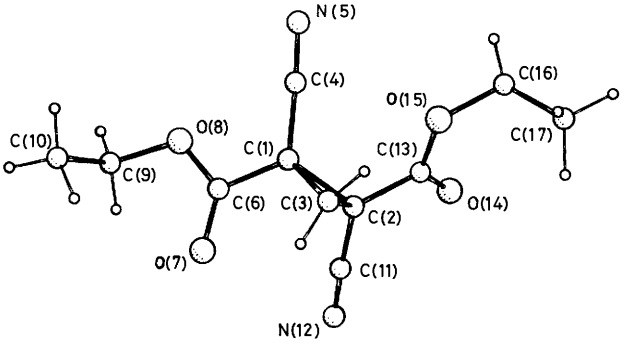


Figure 2. View of compound (**2**) and atom numbering[19]

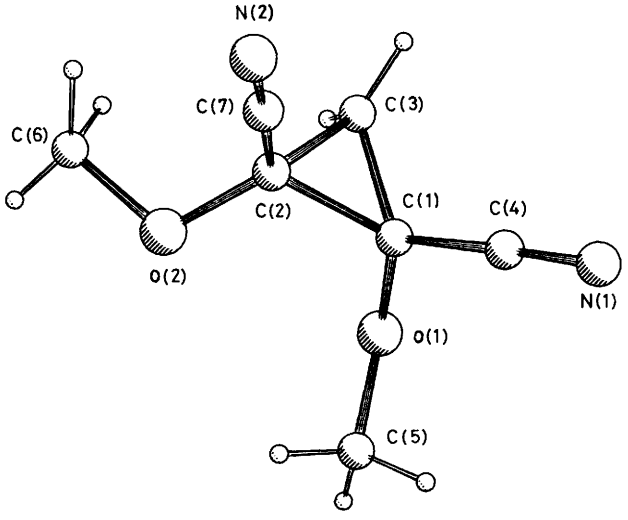


Figure 3. View of compound (**3**) and atom numbering[19]

of the angles around C(1) and C(2) are unexpectedly different: NC–C(1)–COOEt = 115.9(2)° while NC–C(2)–COOEt = 112.0(2)° in (**2**); MeO–C(1)–C(3) = 116.2(2)° while MeO–C(2)–C(3) = 121.5(3)° for (**3**).

Cyclopropane Ring Bond Lengths.—The focal point of this study is the analysis of substituent effects on the ring bond lengths of cyclopropanes. It is important to realise that this group of molecules is unique, because steric effects between substituents are minimized. Substituent-induced bond length variations in cyclopropane derivatives have been surveyed in detail by Allen.[2] We have used his formalism to express the bond length variations. The asymmetry parameter δ is defined as the lengthening (positive δ) or the shortening (negative δ) of the distal (2,3) bond relative to the average Δ ring bond length in Å (Figure 6). The vicinal bonds 1,2 and 1,3 are each modified by $-\frac{1}{2}\delta$. Correspondingly we have assumed that the substituent effects are additive: the bond-length asymmetry in multiple substituted cyclopropanes is the sum of the asymmetries induced by each individual substituent[24,25] (Figure 7).

The ring bond-lengths of the five new derivatives (**1**)—(**5**) together with those of six homologous cd-substituted cyclopropanes already published[1,3–5] are summarized in Table 8. For each compound we have presented the average ring bond-length Δ and the difference δ_{obs} between this mean and each of the ring bonds.

The range of the 11 mean C–C_{ring} distances Δ [1.503(2)—1.528(3) Å] is in agreement with that observed for 81 derivatives (1.469—1.535 Å).[2] The average of the Δ values, 1.513(1) Å, agrees very well with the distances observed in free cyclopropane: 1.510(2) Å by electron diffraction;[26] 1.514(2) Å by

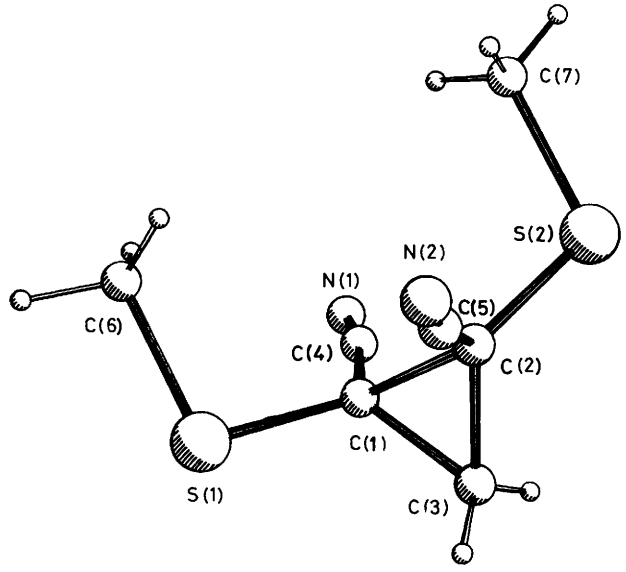


Figure 4. View of compound (**4**) and atom numbering[19]

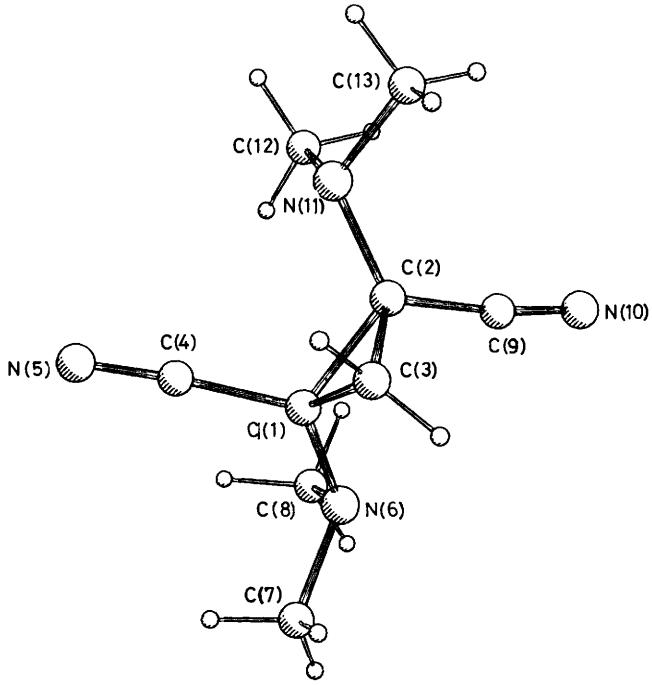
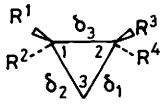


Figure 5. View of compound (**5**) and atom numbering[19]

Table 8. Ring bond lengths (*D*) and asymmetry parameters (δ) in cd-substituted cyclopropanes



*D*1 = C(2)–C(3) Å
*D*2 = C(1)–C(3) Å
*D*3 = C(1)–C(2) Å

δ_{obs}
δ1 = *D*1 − Δ (Å × 10^3)
δ2 = *D*2 − Δ
δ3 = *D*3 − Δ

$$\Delta = \frac{D1 + D2 + D3}{3}\ (\text{Å})$$

δ_{calc}(Å × 10^3)
Σ asymmetry parameters of each substituent (Table 9)
i.e. (1) δ1 = δCN − ½δCN
δ2 = δCN − ½δCN
δ3 = −½δCN − ½δCN

									δ1		δ2		δ3	
No.	R^1	R^2	R^3	R^4	*D*3	*D*2	*D*1	Δ	obs	calc	obs	calc	obs	calc
(**1**)	CN	Me	CN	Me	1.521(2)	1.486(2)	1.503(2)	1.503(2)	0	−9	−17	−9	18	18
(**2**)[a]	CN	COOEt	COOEt	CN	1.568(3)	1.510(3)	1.507(3)	1.528(3)	−21	−20	−18	−20	40	40
(**3**)	CN	OMe	CN	OMe	1.538(4)	1.483(4)	1.493(4)	1.505(4)	−12	−17	−22	−17	33	33
(**4**)	CN	SMe	SMe	CN	1.551(5)	1.499(4)	1.503(4)	1.518(4)	−15	−19	−19	−19	33	37
(**5**)	CN	NMe_2	NMe_2	CN	1.534(3)	1.498(3)	1.502(3)	1.511(3)	−9	−11	−13	−11	23	23
(**6**)[b]	CN	COOMe	SBu^t	CN	1.580(4)	1.491(4)	1.503(4)	1.525(4)	−22	−21	−34	−17	55	39
(**7**)[b]	CN	SPh	SBu^t	CN	1.557(5)	1.507(6)	1.510(5)	1.525(5)	−15	−19	−18	−19	32	37
(**8**)[b]	CN	Ph	SBu^t	CN	1.555(5)	1.503(6)	1.505(6)	1.521(6)	−16	−16	−18	−20	34	36
(**9**)[c]	Cl	COOMe	SBu^t	CN	1.545(5)	1.477(6)	1.506(5)	1.509(5)	−3	−3	−32	−26	36	30
(**10**)[d]	CN	SPh	SMe	CN	1.535(12)	1.501(11)	1.506(12)	1.514(12)	−8	−19	−13	−19	21	37
(**11**)[e]	SPh	CN	SPh	CN	1.561(6)	1.493(6)	1.501(6)	1.518(6)	−17	−19	−25	−19	43	37
	CN[f]	SBu^t	CN	SBu^t	1.563(8)	1.501(9)	1.531(9)	1.532(9)	−1	−19	−31	−19	31	37

[a] Calculation of librational corrections shows uniform variation on bond lengths (max. 0.004 Å) (P. Roberts and G. M. Sheldrick, XANADU, Program for Crystallographic Calculations, 1975, University of Cambridge). [b] Ref. 3. [c] Ref. 5. [d] Ref. 1. [e] Ref. 4. [f] B. Tinant, J. P. Declercq, and M. Van Meerssche, to be published.

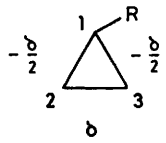


Figure 6. Induced-bond length asymmetry by a single substituent R

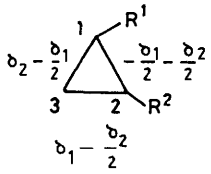


Figure 7. Example of induced-bond length asymmetry for 1,2-disubstituted rings

Raman spectroscopy.[27] Because unexpected variations for the Δ values are observed, the δ_{obs} are obtained by subtracting the mean C–C length from each individual ring increment. Inspection of the δ_{obs} values reported in Table 8 reveals some interesting features. The C–C ring distances are in the range 1.477—1.580 Å with a standard deviation of *ca.* 0.005 Å and the δ_{obs} values vary from −0.034 to +0.055 Å. The asymmetries induced by the substituents are thus significant. Adjacent substituents most probably influence the geometry by conjugative interaction with the cyclopropane ring. The more substituted C(1)–C(2) bond is always the longest: δ_3 values for the 11 derivatives are positive corresponding to a greater C(1)–C(2) bond length than average. The other two bonds [C(1)–C(3) and C(2)–C(3)] are both shorter than the mean value in the 11 derivatives. This observation can be related to our former work which showed the ease of breaking of the C(1)–C(2) bond.[7]

By application of the additivity principle (Figure 7) we have calculated by a least-squares fit of the 33 δ_{obs} values the asymmetry parameters δ_R for R = C≡N, C=O, S–R, Cl, phenyl, OMe, and NMe_2. Their values are reported in Table 8. The results (δ_{calc}) of the summations of the δ_R relative to each bond in each molecule are presented next to the δ_{obs} in Table 8. Some assumptions have been made for these calculations. Only seven different substituents are considered: thus it is assumed that the methyl group has a negligible effect and that COOMe and COOEt on one hand, SMe, SPh, SBu^t on the other, have about the same effect. Moreover the conformations of the substituents have not been taken into account. These approximations seem acceptable with respect to the limited number of compounds and allow thereby some redundancy in the system of equations. Thus it can be seen from comparison of the δ_{calc} with the δ_{obs} ring bond lengths that these are quite well recalculated from the values of the substituent parameters δ_R. Furthermore, the values that we obtained for δ_{CN}, δ_{CO}, δ_{phenyl}, and also to a lesser degree δ_{Cl} are remarkably similar to those deduced by Allen[2] (Table 9). The agreement is of the order of the standard deviation in the bond length for δ_{CN}, δ_{CO}, δ_{phenyl}, and only slightly less good for δ_{Cl} which is calculated from only one compound. There is no possibility of comparison for δ_{SR}, δ_{OMe}, and δ_{NMe_2} but the reproducibility of the other parameters gives an argument for at least the sign of the δ_R. All the three substituents are donors and their δ_R are negative. In other words, these donor substituents induce just as acceptor groups do, a shortening of the distal bond, and a lengthening of the vicinal bonds. These results contrast with the generally expected effect of electron-releasing groups leading to lengthening of the distal bond and shortening of the vicinal ones in cyclopropanes.

There is now ample evidence that the effect of π-acceptor substituents is a shortening of the distal bond and a lengthening of the vicinal bonds. The understanding is that electron density is transferred from the cyclopropane 3e′ orbital to low-lying π-orbitals of the acceptor.[25] Orbital mixing weakens the vicinal bonds for which the 3e′ orbital has bonding character but strengthens the distal bond for which the 3e′ orbital is antibonding. Moreover it has been shown that this effect depends on the conformation of the substituent. Maximum overlap occurs when the π-acceptor group bisects the cyclopropyl ring plane. The results that we have obtained for δ_{CN}, δ_{CO}, and δ_{phenyl} confirm this assumption.

Table 9. Asymmetry parameters δ_R of substituents (Å)

	This study	Allen[2]
CN	−0.018(6)	−0.017(2)
CO	−0.022(7)	−0.026(5)
SR	−0.020(6)	
Cl	0.000(9)	0.012(7)
Phenyl	−0.017(8)	−0.018(2)
OMe	−0.016(8)	
NMe_2	−0.005(8)	

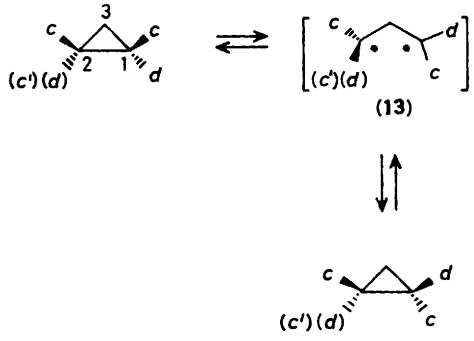
Allen has also shown that the particular donor groups Cl and F have the reverse effect of π-acceptors: lengthening of the distal bond and shortening of the vicinal bonds, while the effect of Br_2 was minimal. We obtained a value of $\delta_{Cl} = 0$ in relatively good agreement with the value deduced by Allen ($\delta_{Cl} = +0.012$ Å) but the effect of π-donors is not clear yet because there was only one Cl substituent in our series and also the negative values that we found for δ_{SR}, δ_{OMe}, and δ_{NMe_2} are surprising. They are in contradiction to the most recent MO calculations [(for cyclopropanone and methylenecyclopropane,[28] and for a variety of fluorocyclopropanes[24,29])] and to the experimental results for halogens. Accordingly the combination of withdrawal of electron density from cyclopropane and donation of electron density from a donor orbital to the $1a_2'$ orbital predicts a pattern opposite to that of π-acceptors. Comparison with experimental data is much more difficult. As Allen has noted,[2] data for donors, except halogens, and for donor–acceptor systems are too sparse for a valid conclusion to be drawn. Most of the 44 structures of O-, N-, or S-substituted cyclopropanes indexed in the Cambridge Data File[30] are spiro or bicyclo systems. Also other substituents with still unknown effects are presented. The best documentation is for *N*-substituted derivatives. The molecular structure of cyclopropylamine has been reinvestigated by microwave spectroscopy[31] and its geometry has been optimized by *ab initio* calculations:[32] both results indicate distal bond lengthening. The cyclopropyl ring bond lengths of 11-morpholino-11-succinimido-*cis*-bicyclo[8.1.0]undecane[33] as observed by *X*-ray crystallography indicate also distal bond lengthening. The results concerning *cis*- and *trans*-cyclopropylbi(dioxopiperazyl)[22] are inconsistent: the distal bond is lengthened in the *trans* isomer but shortened in the *cis* compound. In all these *N*-substituted cyclopropanes the asymmetry induced by NR_2 is small. Some indication of distal lengthening induced by the oxa substituent can also be found, for example in the structures of phorbol[34] or 9-hydroxy-1-methoxy-2-methyltricyclo[5.2.1.$0^{2,10}$]decane *p*-iodobenzoate.[35] In summary MO theory and insufficient experimental results seem to indicate that π-donor groups induce distal bond lengthening.

As our results for δ_{SR}, δ_{OMe}, and δ_{NMe_2} are different from others in the literature, it may be asked whether the additivity principle is valid for donor–acceptor substituted cyclopropanes. Following Jason[36] the substituent effects are not additive for donor–acceptor substitution and in no case has additivity ever

been demonstrated for such compounds. The close similarity of δ_R for R = acceptor that we observed with the values calculated by Allen tends, however, to support the validity of all our results and consequently the additivity principle.

Furthermore, in the case of the 1,2-bis-cd-substituted cyclopropanes (**3**)—(**5**), (**7**), (**9**)—(**12**), conjugation passes through the C(1)–C(2) bond and confers partial olefinic character with bond lengthening.[37,38] Further experiments must decide if additivity results in cd-substituted cyclopropanes. The precise geometry of only donor (SR, OR, or NR_2)-substituted derivatives is still to be measured. Experiments with 1,2-dimethoxy-1,2-dimethyl- and 1,1,2,2-tetrakisphenylthio-cyclopropane are now in progress.

As briefly mentioned above, the structural data here are also of interest in relation to our kinetic study[7] of the *cis–trans* isomerization of substituted cyclopropanes. Three-membered rings carrying cd-substituents (d = OR, SR, c = CN) on both C(1) and C(2) isomerize with exceptionally low activation energies (E_a 24—27 kcal mol^{-1}). The replacement of one cd-couple on C(2) by a dicapto couple in compound (**6**) (c = CN, c′ = COOMe) significantly increases the energy barrier (E_a 31 kcal mol^{-1}). This was attributed to the greater capacity of cd-substituents to stabilize the diradical transition state (**13**) (Scheme 6). The substituents, however, can also modify the



Scheme 6.

ground-state energy. The present *X*-ray study is the first attempt to gain information on the ground state of these cyclopropanes.

It is noteworthy that the highest activation energy and also the longest C(1)–C(2) bond was found for compound (**6**) with cc- and cd-substitution. At this stage we cannot decide how these changes on the cyclopropane bond lengths are related to the ground-state energy changes. The particularly easy isomerization of those cyclopropanes appears best explained, not as the consequence of a destabilized ground state, but rather of increased spin delocalization in the transition state.

Conclusions.—We have determined by *X*-ray analysis the geometry of five new cd- or cc-substituted simple monocyclic cyclopropanes. Their ring bond length values when joined with those of six other known cd-substituted structures[1,3–5] produce a data set of 11 molecules permitting a quantitative study of substituent effects on cyclopropanes. This analysis follows prior methodology[2] and shows that both donor substituents SR, OMe, and NMe_2 and π-acceptor groups CN, COOR, and neutral phenyl groups cause distal bond shortening and vicinal bond lengthening. The values obtained for π-acceptors are: δ_{CN} −0.018, δ_{CO} −0.022 Å and for δ_{phenyl} −0.017 Å and they are in perfect agreement with results of Allen and confirm the effect of electron-withdrawing substituents which had been explained by MO theory[25] and largely demonstrated in published π-acceptor-substituted structures. The values observed for the donor groups δ_{SR} −0.020, δ_{OMe} −0.016, and δ_{NMe_2} −0.005 Å are not directly comparable with published data because there is a lack of solely donor-substituted structures. Our results are however in disagreement with the most recent MO calculations.[24–28] As long as the additivity of substituent effects is not yet demonstrated for *gem* and vicinal donor–acceptor substitution it is impossible to conclude on the effect of donor groups in general.

By comparison of cd- and cc-substituted cyclopropanes we have shown that the captodative couples (SR,CN, OMe,CN, NMe_2,CN) and also dicapto couples cause a shortening of the distal bond and lengthening of vicinal bonds. In both cases, electron density is transferred from the cyclopropyl ring to the substituents. The consequence is that the C(1)–C(2) bond cd- or cc-substituted on C(1) and C(2) is particularly weakened. If the values of the asymmetry parameters of the donor groups are confirmed for purely donor-substituted cyclopropanes two important conclusions would emerge. The first would be that the effects of the substituents on the ring bond lengths are additive even in the case of donor–acceptor substitution. If confirmed it could be concluded also that there is no particular captodative substitution effect in the ground state.

References

1 Part 4, B. Tinant, J. P. Declercq, and M. Van Meerssche, *Bull. Soc. Chim. Belg.*, 1984, **93**, 921.
2 F. H. Allen, *Acta Crystallogr.*, 1980, **B36**, 81.
3 B. Tinant, S. Wu, J. P. Declercq, M. Van Meerssche, A. De Mesmaeker, W. Masamba, R. Merényi, and H. G. Viehe, *J. Chem. Soc., Perkin Trans. 2*, 1985, 535.
4 B. Tinant, J. P. Declercq, and M. Van Meerssche, *J. Chem. Soc., Perkin Trans. 2*, 1985, 541.
5 B. Tinant, J. P. Declercq, and M. Van Meerssche, *Acta Crystallogr.*, 1985, **C41**, 597.
6 H. G. Viehe, R. Merényi, L. Stella, and Z. Janousek, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 917; H. G. Viehe, Z. Janousek, R. Merényi, and L. Stella, *Acc. Chem. Res.*, 1985, **18**, 148.
7 (*a*) A. De Mesmaeker, L. Vertommen, R. Merényi, and H. G. Viehe, *Tetrahedron Lett.*, 1982, **23**, 2369; (*b*) R. Merényi, A. De Mesmaeker, and H. G. Viehe, *Tetrahedron Lett.*, 1983, **24**, 2765.
8 A. Jenczyk and M. Makosza, *Synthesis*, 1976, 387.
9 (*a*) A. De Mesmaeker, Ph.D. Thesis, University of Louvain-la-Neuve, 1983; (*b*) W. Masamba, Ph.D. Thesis, University of Louvain-la-Neuve, Belgium, 1987.
10 L. L. McCoy, *J. Am. Chem. Soc.*, 1962, **84**, 2246.
11 Y. Ito, K. Konezawa, and T. Saegusa, *J. Org. Chem.*, 1974, **39**, 1763.
12 K. D. Gundermann and E. Rohrl, *Justus Liebigs Ann. Chem.*, 1974, 1661.
13 K. Utimoto, Y. Wakabayashi, Y. Shishiyama, M. Inone, and H. Nozaki, *Tetrahedron Lett.*, 1981, **22**, 4279.
14 M. W. Rathke and A. Lindert, *J. Am. Chem. Soc.*, 1971, **93**, 4605.
15 S. Mignani, F. Lahousse, R. Merényi, Z. Janousek, and H. G. Viehe, *Tetrahedron Lett.*, 1985, **26**, 4607.
16 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, 1980 MULTAN 80, A System of Computer Programmes for the Automatic Solution of Crystal Structures from *X*-Ray Diffraction Data, Universities of York and Louvain-la-Neuve.
17 G. M. Sheldrick, 1985, SHELX 86, in 'Crystallographic Computing 3,' eds. G. M. Sheldrick, C. Krüger, and R. Goddard, Oxford University Press, pp. 175—189.
18 G. M. Sheldrick, 1976, SHELX 76, program for crystal structure determination, University of Cambridge.
19 S. Motherwell and W. Clegg, 1978, PLUTO, University of Cambridge.
20 F. H. Allen, *Acta Crystallogr.*, 1981, **B37**, 890.
21 M. Kimura, M. A. Ward, W. H. Watson, and C. E. Venier, *Acta Crystallogr.*, 1979, **B35**, 3122.
22 A. Hempel, N. Camerman, and A. Camerman, *J. Am. Chem. Soc.*, 1982, **104**, 3456.
23 A. C. Haltiwanger, J. M. Burns, G. C. Crockett, and T. H. Koch, *J. Am. Chem. Soc.*, 1978, **100**, 5110.
24 C. A. Deakyne, L. C. Allen, and N. C. Craig, *J. Am. Chem. Soc.*, 1977, **99**, 3895.

25 R. Hoffmann and R. B. Davidson, *J. Am. Chem. Soc.*, 1971, **93**, 5699.
26 O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, 1964, **17**, 538.
27 R. J. Butcher and W. J. Jones, *J. Mol. Spectrosc.*, 1973, **47**, 64.
28 C. A. Deakyne, L. C. Allen, and W. W. Laurie, *J. Am. Chem. Soc.*, 1977, **99**, 1343.
29 A. Skancke, E. Flood, and J. E. Boggs, *J. Mol. Struct.*, 1977, **40**, 263.
30 F. H. Allen, S. Bellard, M. D. Brice, B. A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B. G. Hummeling-Peters, O. Kennard, W. D. S. Motherwell, J. R. Rodgers, and D. G. Watson, *Acta Crystallogr.*, 1979, **B35**, 2331.
31 S. N. Mathur and M. D. Harmony, *J. Chem. Phys.*, 1978, **69**, 4316; M. D. Harmony, R. E. Bostrom, and D. K. Hendrickson, *J. Chem. Phys.*, 1975, **62**, 1599.
32 A. Skancke and J. E. Boggs, *J. Mol. Struct.*, 1978, **50**, 173.
33 E. Vilsmaier, C. M. Klein, D. Dansmann, and G. Maas, *Chem. Ber.*, 1982, **115**, 1209.
34 F. Brandl, M. Rohrl, K. Zechmeister, and W. Hoppe, *Acta Crystallogr.*, 1971, **B27**, 1718.
35 D. Caine, H. Deutsch, S. T. Chao, D. G. Van Derveer, and J. A. Bertrand, *J. Org. Chem.*, 1978, **43**, 1114.
36 M. E. Jason, J. C. Galluci, and J. A. Ibers, *Isr. J. Chem.*, 1981, **21**, 95.
37 R. Hoffmann, *Acc. Chem. Res.*, 1971, **4**, 1.
38 D. L. Kleyer, R. C. Haltiwanger, and T. H. Koch, *J. Org. Chem.*, 1983, **48**, 147.

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