C(8a)—C(4a)—C(4), traduit l'inégalité des interactions du doublet libre de N(1) et des électrons $\pi$ de C(4)—O(14) avec les électrons $\pi$ de C(2)—C(3) d'une part et ceux du cycle *B* d'autre part. Dans ce dernier, les distances C—C entre atomes voisins ont pour longueurs extrêmes 1,353 (3) et 1,411 (2) Å [moyenne: 1,393 (9) Å]. La longueur inhabituelle de la liaison carbonyle C(4)—O(14) [1,261 (2) Å] paraît en relation avec l'existence de la liaison hydrogène O(13)—H(13)···O(14). C(6)—F(15) [1,362 (2) Å] n'est pas significativement différente de la liaison C—F présente dans l'acide *o*-fluorobenzoique (1,368 Å) (Wyckoff, 1969). Bien que légèrement courtes, les liaisons $Csp^3$—$Csp^3$ C(9)—C(10), C(17)—C(18) et C(20)—C(21) peuvent être considérées comme normales. Il en est de même des liaisons du groupement carboxylique.

Les distances N—C peuvent être classées en deux groupes. N(1)—C(9), N(16)—C(17), N(16)—C(21) et les trois liaisons issues de N(19) ont des longueurs comprises entre 1,453 (2) et 1,490 (2) Å. Ce sont des liaisons simples. N(1)—C(2), N(1)—C(8a) et N(16)—C(17) sont du même ordre que les liaisons N—C rencontrées dans la pyridine (1,3402 Å) (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958). La longueur de N(16)—C(17) [1,388 (2) Å] indique la conjugaison du doublet non partagé de N(16) et des électrons $\pi$ du cycle *B*.

Une liaison hydrogène N—H···O et quatre liaisons O—H···O participent à la cohésion de la structure. Leurs longueurs et leurs angles sont rapportés dans le Tableau 2.

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# Substituted Cyclopropanes. 7. *cis* and *trans* Isomers of 1,2-Cyclopropanedicarboxylic Acid*


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**Abstract.** $C_5H_6O_4$, $M_r = 130{\cdot}10$. *trans* isomer: monoclinic, $C2/c$, $a = 9{\cdot}408$ (2), $b = 4{\cdot}9696$ (10), $c = 12{\cdot}578$ (2) Å, $\beta = 98{\cdot}93$ (2)°, $V = 581{\cdot}0$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}49$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}1$ mm$^{-1}$, $F(000) = 272$, $T = 293$ K; $R = 0{\cdot}048$ for 544 unique observed reflections. *cis* isomer: monoclinic, $P2_1/n$, $a = 5{\cdot}374$ (2), $b = 11{\cdot}115$ (2), $c = 9{\cdot}741$ (2) Å, $\beta = 96{\cdot}43$ (2)°, $V = 578{\cdot}2$ Å$^3$, $Z = 4$,


* Part 6: Jones & Schrumpf (1987*c*).

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$D_x = 1{\cdot}49$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu$ = 0·1 mm$^{-1}$, $F(000) = 272$, $T = 293$ K; $R = 0{\cdot}047$ for 837 unique reflections. In the *trans* isomer, which displays crystallographic twofold symmetry, the carboxyl groups are close to a *cis* bisected conformation. In the *cis* isomer, one carboxyl group adopts a *cis* bisected, the other a synclinal conformation. The marked ring-bond asymmetry in both isomers is in accordance with simple molecular-orbital considerations. Both isomers display the pairwise hydrogen bonding typical of carboxylic acids.

**Introduction.** We have recently determined the crystal structures of a number of cyclopropane derivatives (Jones & Schrumpf, 1987*a,b,c*; Schrumpf & Jones, 1987*a,b,c*). We found that both electronic and steric effects determine the substituent-induced asymmetry of the cyclopropane ring. In triethyl *trans*-1,2,3-tricyano-1,2,3-cyclopropanetricarboxylate (Jones & Schrumpf, 1987*c*) the conformations of the ester groups affect the ring bonds differently, reflecting the varying extent of conjugation between the ester groups and the ring.

Additivity of the electronic effects of several substituents (Hoffmann & Stohrer, 1971) was inferred from a critical survey of many, mostly heavily substituted, cyclopropane derivatives (Allen, 1980). However, structures of simple 1,2-disubstituted cyclopropanes are needed to test this hypothesis further. The only symmetrical 1,2-disubstituted cyclopropanes studied so far are *trans*-1,2-divinylcyclopropane (Trætteberg, Almenningen, Schrumpf & Martin, 1987) and *trans*-1,2-bis($\beta$-carbethoxyvinyl)cyclopropane (Dekaprilevič & Vorontsova, 1975). In the former case, the additivity effect could not be reliably studied because of the complicated conformational equilibrium in the vapour phase.

We have therefore studied the crystal structures of *cis*- and *trans*-1,2-cyclopropanedicarboxylic acids, which are two of the few simple 1,2-disubstituted cyclopropanes that are solid at ambient temperatures and that are expected to be conformationally frozen in the crystal. One modification of the *trans* isomer has already been studied (Bednowitz, 1969) but with insufficient precision for our purposes (bond-length e.s.d.'s *ca* 0·008 Å).

**Experimental.** The two isomeric title compounds were synthesized by literature methods (McCoy, 1958). The stereochemistry was proved by NMR spectroscopy. Suitable crystals of the *trans* isomer were grown from acetone/1,1,2,2-tetrachloroethane and of the *cis* isomer from dichloromethane/acetonitrile, in both cases by liquid–liquid diffusion. Both compounds formed colourless prisms. The *trans* isomer crystallized in a different modification from that previously studied (Bednowitz, 1969). The cell constants of the present modification have already been reported (Hofmann, Orochena, Sax & Jeffrey, 1959) and agree well with our data (see below).

[In the description of the structure determinations that follows, values for the *trans* isomer are given first, those for the *cis* isomer (where different) being given in braces.] Crystal 0·4 × 0·25 × 0·25 mm {0·6 × 0·4 × 0·2 mm}, mounted about 102 {100}. Stoe–Siemens four-circle diffractometer, monochromated Mo $K\alpha$ radiation, profile-fitting mode (Clegg, 1981). $2\theta_{max}$ 55° {50°}, hemisphere $\pm h+k\pm l$ {quadrant $-h+k\pm l$ and some $+h$ equivalents}. Three check reflections, no intensity change. 1414 intensities, 664 unique, 544 with $F > 4\sigma(F)$ used for all calculations {1581, 1023, 837}. $R_{int}$ 0·022 {0·025}; index ranges after merging $|h| \le 12$, $|k| \le 6$, $|l| \le 16$ {6,13,11}. Cell constants refined from $2\theta$ values of 42 reflections in the range 20–23°.

Structure solution by routine direct methods. Anisotropic full-matrix refinement on $F$ to $R$ 0·048, $wR$ 0·051 {0·047, 0·051}. 54 {100} parameters, weighting scheme $w^{-1} = \sigma^2(F) + gF^2$ with $g = 0{\cdot}00025$ {0·0002}. H atoms refined freely {C—H refined with $U(H) = 1{\cdot}2 \times U_{eq}(C)$, O—H with corresponding constraint and with a fixed bond length of 0·96 Å}. $S = 2{\cdot}04$ {1·95}, max. $\Delta/\sigma$ 0·001 {0·026}, max. features in final $\Delta\rho$ map +0·16, −0·22 e Å$^{-3}$. Atomic scattering factors as incorporated in program systems *SHELX*76, *SHELXTL* (Sheldrick, 1976, 1978).

**Discussion.** Final atomic coordinates and derived parameters are given in Tables 1–4.* Rigid-body libration corrections were attempted but gave unsatisfactory $R_{lib}$ values (>0·1), presumably because of torsional freedom. All bond lengths are therefore uncorrected.

The two isomers have markedly different bond lengths and conformations and will thus be discussed separately.

*trans-1,2-Cyclopropanedicarboxylic acid.* The molecule possesses crystallographic twofold symmetry, C(1) lying on the axis 0·5, *y*, 0·25 (Fig. 1). The unique carboxyl group adopts an almost *cis*-bisected (*cb*) conformation [10° off the plane through C(21), C(2), and the midpoint of C(1)–C(2$^i$)] with the carbonyl oxygen eclipsing the ring, as expected in carbonyl-substituted cyclopropanes. This is close to the conformation for optimum conjugation between the carboxyl groups and the ring. The slight rotation of the carboxyl groups away from the ideal conformation has precedents in the similar deviation from $C_s$ symmetry in cyclopropylcarboxamide (Long, Maddox & Trueblood, 1969), cyclopropylhydrazide (Chesnut & Marsh,

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43948 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atom coordinates* ($\times 10^4$) *and isotropic temperature factors* ($Å^2 \times 10^3$) *for the trans isomer*

| | x | y | z | $U/U_{eq}$ |
|---|---|---|---|---|
| C(1) | 5000 | −2393 (5) | 2500 | 43 (1)* |
| C(2) | 5157 (2) | 176 (4) | 1921 (1) | 37 (1)* |
| C(21) | 3976 (2) | 1112 (4) | 1087 (1) | 36 (1)* |
| O(1) | 2714 (1) | 382 (3) | 1097 (1) | 57 (1)* |
| O(2) | 4367 (1) | 2716 (3) | 392 (1) | 55 (1)* |
| H(1) | 5943 (24) | −3382 (54) | 2760 (18) | 70 (7) |
| H(2) | 6087 (21) | 774 (36) | 1830 (15) | 43 (5) |
| H(O2) | 3602 (29) | 3491 (64) | −141 (22) | 123 (11) |

*Equivalent isotropic $U$ calculated from anisotropic $U$: $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

Table 2. *Atom coordinates* ($\times 10^4$) *and isotropic temperature factors* ($Å^2 \times 10^3$) *for the cis isomer*

| | x | y | z | $U/U_{eq}$ |
|---|---|---|---|---|
| C(1) | 5438 (4) | 1996 (2) | 3971 (2) | 46 (1)* |
| C(2) | 4175 (4) | 2060 (2) | 2504 (2) | 49 (1)* |
| C(3) | 6031 (5) | 2981 (2) | 2997 (2) | 56 (1)* |
| C(11) | 7363 (4) | 1090 (2) | 4374 (2) | 41 (1)* |
| O(11) | 8876 (3) | 761 (1) | 3602 (1) | 59 (1)* |
| O(12) | 7336 (3) | 696 (1) | 5628 (1) | 51 (1)* |
| C(21) | 4653 (4) | 1171 (2) | 1434 (2) | 45 (1)* |
| O(21) | 6247 (3) | 1318 (1) | 643 (1) | 65 (1)* |
| O(22) | 3164 (3) | 262 (1) | 1354 (2) | 73 (1)* |
| H(1) | 4386 (42) | 2207 (18) | 4651 (22) | 55 |
| H(2) | 2561 (47) | 2202 (20) | 2489 (21) | 57 |
| H(3a) | 7666 (48) | 2886 (22) | 2622 (23) | 66 |
| H(3b) | 5415 (46) | 3747 (22) | 3174 (24) | 66 |
| H(12) | 8724 | 153 | 5810 | 62 |
| H(22) | 3559 | −259 | 623 | 87 |

*Equivalent isotropic $U$ calculated from anisotropic $U$: $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

Table 3. *Bond lengths* (Å) *and angles* (°) *for the trans isomer*

| | | | |
|---|---|---|---|
| C(1)–C(2) | 1·488 (3) | C(2)–C(21) | 1·480 (2) |
| C(21)–O(1) | 1·243 (2) | C(21)–O(2) | 1·278 (2) |
| C(2)–C(2$^i$) | 1·530 (3) | | |
| C(21)–C(2)–C(1) | 119·7 (1) | C(2)–C(1)–C(2$^i$) | 61·9 (2) |
| O(1)–C(21)–C(2) | 120·9 (2) | O(2)–C(21)–C(2) | 114·6 (1) |
| O(2)–C(21)–O(1) | 124·5 (2) | C(21)–C(2)–C(2$^i$) | 116·1 (2) |
| C(1)–C(2)–C(2$^i$) | 59·1 (2) | | |

Symmetry operator (i): $1-x, y, 0{\cdot}5-z$.

Table 4. *Bond lengths* (Å) *and angles* (°) *for the cis isomer*

| | | | |
|---|---|---|---|
| C(1)–C(2) | 1·514 (4) | C(1)–C(3) | 1·505 (4) |
| C(1)–C(11) | 1·465 (4) | C(2)–C(3) | 1·471 (4) |
| C(2)–C(21) | 1·480 (4) | C(11)–O(11) | 1·224 (4) |
| C(11)–O(12) | 1·300 (3) | C(21)–O(21) | 1·225 (4) |
| C(21)–O(22) | 1·286 (4) | | |
| C(2)–C(1)–C(3) | 58·3 (2) | C(2)–C(1)–C(11) | 120·9 (3) |
| C(3)–C(1)–C(11) | 118·4 (3) | C(1)–C(2)–C(3) | 60·6 (2) |
| C(1)–C(2)–C(21) | 122·6 (3) | C(3)–C(2)–C(21) | 122·0 (3) |
| C(1)–C(3)–C(2) | 61·1 (2) | C(1)–C(11)–O(11) | 122·6 (3) |
| C(1)–C(11)–O(12) | 113·7 (3) | O(11)–C(11)–O(12) | 123·7 (3) |
| C(2)–C(21)–O(21) | 122·8 (3) | C(2)–C(21)–O(22) | 114·3 (3) |
| O(21)–C(21)–O(22) | 122·8 (3) | | |

1958), 1,1-cyclopropanedicarboxylic acid (Meester, Schenk & MacGillavry, 1971) and *trans*-2,*trans*-3-dimethylcyclopropanecarboxylic acid (Luhan & McPhail, 1972).

The difference in the ring bond lengths, C(2)–C(2$^i$) 1·530 and C(1)–C(2) 1·488 Å, is qualitatively and quantitatively as expected for strong $\pi$-electron acceptors. The mean length is 1·502 Å. In the earlier modification (Bednowitz, 1969) the mean bond distance, 1·501 Å, is almost the same but the long bond (1·518 Å) is shorter than in the present molecule; this difference is, however, of marginal significance. The carboxyl groups in the earlier study also adopted a *cis*-bisected conformation (corresponding torsion angles −6·3, +0·7°).

In order to test the additivity of the carboxyl group effects on the ring geometry in a quantitative manner, the data for cyclopropanecarboxylic acid would serve as a basis for comparison. Unfortunately, no crystal structure of the low-melting monoacid has been published. However, two simple acid derivatives, the carboxamide and the hydrazide, and also the dimethylcyclopropanecarboxylic acid (see above) could be used as comparisons. The average shortening of the distal bonds is 0·023 Å and the average lengthening of the lateral bonds is 0·012 Å. We would thus predict, if

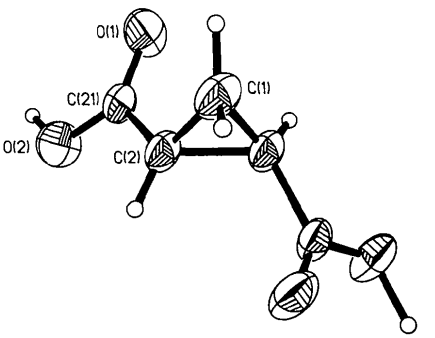


Fig. 1. Thermal-ellipsoid plot (50% level) of the *trans* isomer, showing the numbering scheme of the asymmetric unit.

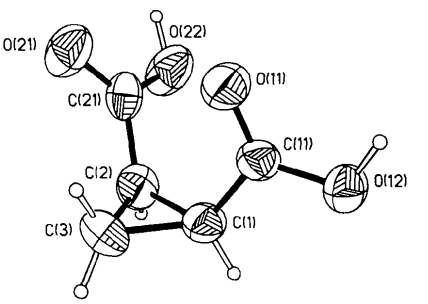


Fig. 2. Thermal-ellipsoid plot (50% level) of the *cis* isomer, showing the atom-numbering scheme.

additivity is valid, bond lengths of 1·526 and 1·491 Å in the present 1,2-disubstituted compound; this is in good agreement with the experimental values.

The two exocyclic C—C bonds (1·480 Å) are somewhat longer than in the dimethyl-substituted monoacid [1·456 (6) Å] but essentially the same as in the 1,1-diacid (average of four values: 1·484 Å) and the 1-cyanoacid [1·490 (4) Å (Jones & Schrumpf, 1987*b*)].

*cis*-1,2-*Cyclopropanedicarboxylic acid* (Fig. 2). The two carboxyl groups in the *cis* isomer would be expected to display different effects from those of the *trans* isomer because of steric strain. The conformations of these groups, which are the parameters most sensitive to intramolecular steric interactions, are indeed different. The substituent at C(1) adopts a *cb* conformation (torsion angle 2°) with the carbonyl oxygen eclipsing the ring, as is usual in carbonyl-substituted cyclopropanes. However, the second group, at C(2), is rotated from the *cb* position by 55°, still with the carbonyl oxygen above the ring (*sc* conformation).

The conformational difference between the two carbonyl groups is presumably of steric origin. The interference between the two *cisoid* carbonyl oxygen atoms O(11) and O(21) leads to the observed $C_1$ structure in the crystal, with two non-equivalent acid groups. $C_s$ geometry, with two equivalent carboxyl groups rotated by the same angle from the *cb* form, is not attained, probably because the conjugative electronic energy gain by one *cb* carboxyl group in the $C_1$ form is substantial. Alternatively, crystal packing might be more favourable for the $C_1$ form, although such assertions are difficult to prove.

The conformations of the carboxyl groups have a pronounced effect on the ring bond lengths. The bond C(2)—C(3) opposite the *cb* substituent is shortened (1·471 Å) as expected for a $\pi$-electron acceptor. Since the conjugative interaction of the second carboxyl group (*sc*) is weak, we observe no significant shortening of the bond C(1)—C(3) opposite this group (1·505 Å). The difference between the bond lengths C(1)—C(2), 1·514 Å, and C(1)—C(3) is *ca* three e.s.d.'s. If this is significant, it may be associated with the slight $\pi$-electron withdrawal or an inductive effect of the carboxyl groups, or even an elongation of C(1)—C(2) by steric repulsion between the substituents. We plan to study appropriate model compounds in order to determine the effect of an *sc* or *p* carboxyl group on a cyclopropane ring.

The difference between the two acid groups is also reflected in the bond lengths C(1)—C(11), 1·465, and C(2)—C(21), 1·480 Å; the conjugative interaction shortens the former. A correspondingly short bond is also seen in the dimethyl-substituted acid (1·456 Å). However, the bonds in the *trans* diacid (1·480 Å) are not consistent with this pattern, although they also interact with the ring. This may reflect the competition of two equivalent *cb* carbonyl groups for ring electrons.

Steric interactions are apparent from several bond angles. In the *trans* isomer, the average bond angle of C(21)—C(2)—C(1) and C(21)—C(2)—C(2$^{i}$), which defines the inclination of the substituent towards the cyclopropane ring plane, is 117·9°. In the *trans* dimethyl-substituted acid, the average such bond angle is 120·1° and in *trans*-2-pivaloylcyclopropanecarboxylic acid 118·3° (Roques, Crasnier, Declercq, Germain, Cousse & Mouzin, 1982). In the *cis* diacid, the corresponding value for the *cb* carboxyl group is 119·7° but for the *sc* group 122·3°. The angular deformation of the unconjugated *sc* carboxyl group appears to be easier than that of the *cb* group.

*Molecular packing.* Both isomers display the usual carboxylic acid pairwise hydrogen bonding across centres of symmetry. In the *trans* isomer (Fig. 3) the hydrogen bond is O(2)···O(1) (at $0{\cdot}5-x$, $0{\cdot}5-y$, $-z$), 2·66 (1) Å. The molecules are linked in chains in the direction [101].

In the *cis* isomer, the hydrogen bonds are O(12)··· O(11) (at $2-x$, $-y$, $1-z$) 2·65 (1) and O(22)···O(21) (at $1-x$, $-y$, $-z$) 2·67 (1) Å. The molecules are linked in chains in the direction [101] (Fig. 4).

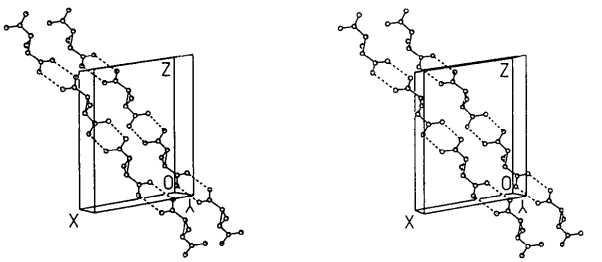


Fig. 3. Packing plot of the *trans* isomer, showing the hydrogen bonds (dashed lines). H atoms omitted.

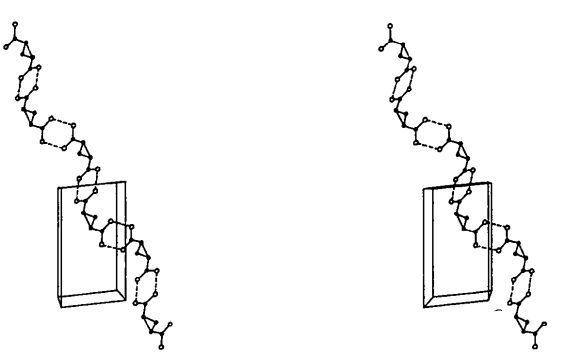

Fig. 4. One of the hydrogen-bonded chains of the *cis* isomer (hydrogen bonds indicated by dashed lines). H atoms omitted. View direction along **b**, **a** horizontal, **c** vertical.

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# Substituted Cyclopropanes. 8. 2,2,3,3-Tetramethylcyclopropanecarboxylic Acid*

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**Abstract.** $C_8H_{14}O_2$, $M_r = 142{\cdot}20$, monoclinic, $P2_1/n$, $a = 6{\cdot}3457\ (10)$, $b = 11{\cdot}7207\ (14)$, $c = 11{\cdot}758\ (2)$ Å, $\beta = 104{\cdot}27\ (2)°$, $V = 847{\cdot}5$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}11$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu$(Mo $K\alpha$) $= 0{\cdot}05$ mm$^{-1}$, $F(000) = 312$, $T = 293$ K, $R = 0{\cdot}059$ for 1313 unique observed reflections. The molecule adopts a slightly distorted *cis*-bisected conformation, with the carbonyl oxygen eclipsing the ring. The cyclopropane ring is asymmetric, with one short and two longer bonds, in accordance with theoretical expectations. The absolute values of the bond lengths and several bond angles indicate substantial steric interactions between the carboxyl and the two *cis* methyl groups. The molecules are linked in pairs across centres of symmetry by the usual carboxylic acid hydrogen bonding.

* Part 7: Schrumpf & Jones (1987).

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**Introduction.** The interaction between a cyclopropane ring and a $\pi$-acceptor substituent induces a shortening of the connecting bond and a ring-bond asymmetry, with a short bond opposite the substituent and two longer adjacent bonds. This is documented by many structures of appropriate cyclopropane derivatives determined by X-ray diffraction in the crystalline state and by electron diffraction and rotational spectroscopy in the vapour phase (Allen, 1980). Cyclopropane derivatives of chemical interest are for the most part polysubstituted molecules, and the question arises as to the additivity of these substituent effects. Moreover, since the simple monosubstituted cyclopropanes are mostly liquids at ambient temperatures, crystal structures of those compounds are only feasible at low temperatures, for example cyano- and aminocyclopropane (Kiers, de Boer, Heijdenrijk, Stam & Schenk,