Crystal, Molecular, and Electronic Structure of 13,13-Difluoro-1,7-methano[12]annulene

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The results of an *X*-ray diffraction study of 13,13-difluoro-1,7-methano[12]annulene at room temperature and at 125 K are presented and the crystal, molecular, and electronic structure is discussed. Environmental effects on the structure are discussed by an analysis of the influence of temperature, and by comparison with the geometry of a previously studied bridged [12]annulene.

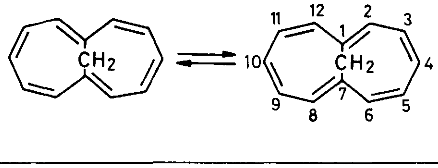
Bridged annulenes constitute a class of compounds where a number of structural features of chemical interest are demonstrated.[1] For example, in dibridged [14]annulenes the ring can show aromatic or polyenic geometry according to the *syn*- or *anti*-position of the two bridges.[2] Another important issue is the fact that in monobridged [10]annulene the effect of substituents at the bridging carbon can push the equilibrium between the annulene and biscaradiene form to either side.[3] The monobridged [12]annulenes, on the other hand, should be a classical case, where the Hückel rule suggests bond alternation, and aromatic behaviour can be safely excluded. To confirm this expectation, the crystal and molecular structure determination of 4,10-dibromo-1,7-methano[12]annulene was carried out some years ago.[4] Indeed, bond alternation along the perimeter shows up very well. The distances of the carbon atoms in the perimeter from the least-squares plane through the annulene ring are <0.35 Å. The dibromo-derivative was used because of the low m.p. of the parent hydrocarbon, but the presence of the two hetero-atoms has been reasonably assumed to have no effect on the ring geometry. When the parent hydrocarbon was studied by ^{13}C n.m.r. spectroscopy at various temperatures,[5] the results were interpreted as experimental evidence of the existence of equilibrium (1) at room temperature, with an activation barrier of *ca.* 5 kcal mol^{-1} for the π bond shift. At low temperature (−135 °C) the spectra clearly indicate freezing of the equilibrium and consistency with C_2 symmetry. It seemed to us that further studies of [12]annulene derivatives might help in understanding the problem, and thus the crystal structure determination of 13,13-difluoro-1,7-methano[12]annulene has been undertaken, both at room and low (*ca.* 125 K) temperature. Professor E. Vogel kindly supplied us with a sample of the compound.

Experimental

Room-temperature Crystallographic Measurements.—The blackish red crystals of the title compound are sensitive to air and/or moisture, but no degradation was observed for crystals sealed in Lindemann glass capillaries; therefore, this protection was adopted for all samples used in the course of the analysis.

A prismatic crystal of approximate dimensions 0.35 × 0.27 × 0.20 mm was used for crystallographic measurements at room temperature (293 ± 2 K). The quality of the specimen was checked by photographic methods, and the crystal was then mounted on a computer-controlled four-circle diffractometer equipped with a graphite monochromator and a scintillation counter (Mo-K_α radiation, $\lambda = 0.7107$ Å).

Lattice parameters at 293 K are reported in Table 1. Systematic absences were consistent with the space group $P2_12_12_1$ (D_2^4, No. 19). Owing to the high reactivity of the substance, no reliable measure of the density could be obtained by flotation methods (values in the range 1.33—1.38 g cm^{-3} were obtained depending on the liquids used for the solution).



(1)

Table 1. Crystal data

Formula $C_{13}H_{10}F_2$	$M = 204.2$
Orthorhombic	Space group $P2_12_12_1$
μ(Mo-K_α) = 1.1 cm^{-1}	$Z = 4$
293 K	125 K
$a = 10.498(2)$ Å	10.427(2) Å
$b = 15.459(3)$	15.280(2)
$c = 6.337(1)$	6.218(1)
$U = 1\,028.4(4)$ Å^3	990.7(3) Å^3
$\rho_{calc} = 1.319$ g cm^{-3}	1.369 g cm^{-3}

Intensity data were collected by the variable-rate θ—2θ scan technique for the three equivalent reciprocal lattice octants *hkl*, $\bar{h}kl$, and $h\bar{k}l$, over the range $2.0 < 2\theta < 55.0°$. The agreement between multiply measured intensities was nearly within the counting statistics. Each reflection was assigned a variance $\sigma^2(I) = \sigma^2(I)_{c.s.} + (0.03S)^2$, where $\sigma^2(I)_{c.s.}$ is the variance derived from counting statistics, and S is the scan count. The intensities and their standard deviations were corrected for Lorentz and polarisation factors, but not for absorption. A merger of the 4 548 data collected yielded 1 393 independent reflections, of which 1 268 having a scan count greater than background were treated as observed.

The structure was solved by using the direct-methods program MULTAN,[6] which gave an E map showing 13 out of the 15 non-hydrogen atoms. Difference maps and geometrical arguments were used to define the co-ordinates of the two missing carbon atoms and the 10 hydrogen atoms, and the model was complete. In the last full-matrix least-squares cycles of refinement, 176 parameters were simultaneously adjusted: positional co-ordinates for the 25 atoms, anisotropic temperature coefficients for the 15 C and F atoms, isotropic B values for the 10 H atoms, and a scale factor. Convergence was assumed when no parameter shift exceeded 10% of its e.s.d. (derived from the diagonal elements of the final least-squares matrix). All 1 268 observed reflections were utilized in the refinement. The final disagreement indices were $R = 0.062$, $R_w = 0.033$, g.o.f. = 1.39.† Positional and thermal parameters

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† The definitions of the R factors are $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R_w = [S/\Sigma wF_o^2]^{\frac{1}{2}}$, and g.o.f. = $[S/(n_{obs} - n_{param})]^{\frac{1}{2}}$, where $S \equiv \Sigma w(|F_o| - |F_c|)^2$, the function minimized in the least-squares refinement using $w = 4F_o^2/\sigma^2(F_o^2)$.

and observed and calculated structure factors are listed in Supplementary Publication No. SUP 23596 (19 pp.).*

The final set of parameters was characterized by extremely high temperature factors for the hydrogen atoms, up to the perhaps unrealistic value of 23(2) Å^2 (corresponding to an r.m.s. amplitude of oscillation of 0.54 Å); moreover, the derived geometry showed severe anomalies (see next section). To check whether these features were somehow related to the sample used for the data collection, a second set of intensities was measured from a different crystal ($2\theta_{\text{max.}}$ = 50.0°; 1 087 reflections, of which 107 with $I < 0$ were given zero weight). Full-matrix least-squares refinement was performed on the set of parameters obtained from the previous investigation. At convergence (maximum parameter shift 0.2σ), R was 0.068, R_w 0.043, and g.o.f. 1.16. Comparison of the two sets of final parameters at room temperature showed a virtual coincidence, the largest differences rarely exceeding 2σ, and then only slightly.

Low-temperature (125 K) *Measurements*.—A third crystal,† a prism of dimensions 0.375 × 0.30 × 0.15 mm, was mounted on the Syntex P$\bar{1}$ diffractometer equipped with the low-temperature LT-1 device. An inclusive error of ±5 K may be safely associated with the temperature measurements, made by an accurately calibrated thermocouple. Unit-cell dimensions at 125 ± 5 K are reported in Table 1. Data collection, reduction, and refinement closely followed the procedure described above for the room-temperature data, except for the portion of reciprocal lattice scanned, here up to 2θ = 60.0°, for a total of 1 691 independent reflections. The 66 net intensities <0 were given zero weight and were not included in the refinement.

For this set of data, the final R index was 0.045, and R_w 0.040; the g.o.f., based on 1 625 reflections and 176 parameters, was 1.28. The final positional parameters are listed in Table 2 and the temperature factors and the observed and calculated structure factors are given in SUP 23596. Atomic scattering factors for C and F were from ref. 7, and for H from ref. 8. No account was taken of anomalous dispersion.

Discussion

The diffraction data have been collected both at room temperature and at 125 K for the sake of comparison with the temperature-dependent n.m.r. spectra. As mentioned in the Experimental section, the refinement of the room-temperature structure led to anomalously high temperature factors, with B values up to 8.5(3) Å^2 for carbon atoms, and 23(3) Å^2 for hydrogen atoms. Indeed, when the anisotropic thermal parameters of the atoms of the annulene ring were interpreted in terms of molecular rigid-body motion,[9] a very poor fit was obtained, the disagreement between observed and calculated values of B_{ij} values being >3σ in most cases. On the other hand, a very satisfactory agreement resulted from the same least-squares treatment of the low-temperature values, which led to mean-square rotational displacements about the principal axes of the L tensor of 14, 11, and 7 (deg)^2. All this, and further points discussed below, suggests that at room temperature the usual Gaussian probability function we have adopted might not provide, for the molecule here studied, an adequate model for atomic thermal motion. The implication would be that the atomic positions, and consequently the interatomic distances, may also be wrongly estimated. For this reason, a detailed discussion of the room-temperature geometry seems inappropriate; only some aspects will be taken up in comparison with the low-temperature structure.

Table 2. Low-temperature (*ca.* 125 K) final positional parameters with estimated standard deviations in parentheses

Atom	x	y	z
C(1)	0.616 7(2)	0.438 68(11)	0.377 3(3)
C(2)	0.737 9(2)	0.413 03(12)	0.423 3(3)
C(3)	0.799 6(2)	0.328 91(14)	0.393 9(4)
C(4)	0.793 3(2)	0.271 47(13)	0.230 1(4)
C(5)	0.727 9(2)	0.273 10(13)	0.024 9(4)
C(6)	0.625 0(2)	0.316 55(12)	−0.055 1(3)
C(7)	0.533 3(2)	0.376 23(12)	0.042 5(3)
C(8)	0.468 5(2)	0.435 02(14)	−0.079 1(3)
C(9)	0.384 5(2)	0.506 62(14)	−0.018 9(4)
C(10)	0.392 2(2)	0.564 37(13)	0.143 3(4)
C(11)	0.486 7(2)	0.578 86(12)	0.311 1(4)
C(12)	0.578 9(2)	0.529 95(12)	0.403 7(3)
C(13)	0.520 8(2)	0.376 04(12)	0.283 3(3)
F(1)	0.536 9(1)	0.293 27(6)	0.363 4(2)
F(2)	0.398 8(1)	0.397 51(7)	0.346 3(2)
H(2)	0.790(2)	0.456(1)	0.491(4)
H(3)	0.860(2)	0.317(1)	0.508(4)
H(4)	0.850(2)	0.221(1)	0.242(4)
H(5)	0.766(3)	0.236(2)	−0.081(5)
H(6)	0.606(2)	0.307(1)	−0.205(4)
H(8)	0.479(2)	0.428(2)	−0.232(4)
H(9)	0.311(2)	0.517(2)	−0.116(5)
H(10)	0.329(2)	0.607(2)	0.144(4)
H(11)	0.485(2)	0.639(2)	0.363(4)
H(12)	0.631(2)	0.558(2)	0.505(4)

Bond distances and angles derived from the structure analysis are listed in Table 3, while torsion angles are given in Table 4. For the 125 K molecular model, an almost perfect local C_2 symmetry is apparent, symmetry-related values being coincident, with a single exception, within 3σ (in most cases 1σ). The same feature is substantially maintained at room temperature, and symmetry-averaged values are reported in the molecular illustrations [10] of Figure 1. At low temperature, an unequivocal alternation of short and long bond distances, which can be related to the cyclic polyenic character of the molecule, is evident. The averaged values of short and long bonds are 1.350(6) and 1.452(4) Å, respectively. The usual tests for aromaticity [11] give values of $\rho = \langle (r_i - \bar{r})^2 \rangle^{\frac{1}{2}} = 0.051$ Å and $\tau = \langle \tau_i^2 \rangle^{\frac{1}{2}} = 21.5°$, where r_i is the observed bond length in the ring, and τ_i the torsion angle in the annulene perimeter. The value of the first quantity is in agreement with the trend shown in previous calculations,[12] which indicated that ρ is usually in the range 0.012—0.024 Å in aromatic annulenes, and >0.03 Å in cyclopolyolefins.

A striking feature of Figure 1 is the very large reduction in the mean molecular motion at 125 K (Figure 1b) compared with room temperature (Figure 1a). In fact, the average mean-square displacements ($\bar{U}_{ii}$) are reduced by factors [3.1(3) for $\bar{U}_{11}$, 3.3(3) for $\bar{U}_{22}$, and 3.4(4) for $\bar{U}_{33}$] much larger than the temperature ratio T_{initial} (293 K)/T_{final}(125 K), 2.34. Such a large reduction is not totally unexpected, in view of the significant contraction of the cell dimensions with temperature (Table 1). Rather interestingly, even at 125 K, no particularly short intermolecular contacts are present; the only two distances close to the sum of van der Waals' radii are reported in the packing illustration of Figure 2. The corresponding values

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1983, Issue 1.

† Attempts to transfer the two crystals used for the room-temperature data collection on mounts suitable for the low-temperature experiment were unsuccessful: optical inspection showed that both crystals had been severely damaged during the manipulations, and therefore they were disregarded.

Table 3. Bond distances and angles with estimated standard deviations in parentheses

(a) Bond distances

	293 K	125 K uncorrected	125 K* corrected
C(1)–C(2)	1.366(4)	1.354(3)	1.358
C(7)–C(8)	1.367(5)	1.355(3)	1.359
C(2)–C(3)	1.387(6)	1.449(3)	1.453
C(8)–C(9)	1.389(6)	1.451(3)	1.455
C(3)–C(4)	1.313(7)	1.346(3)	1.351
C(9)–C(10)	1.326(8)	1.342(3)	1.347
C(4)–C(5)	1.407(8)	1.447(3)	1.452
C(10)–C(11)	1.405(7)	1.452(3)	1.458
C(5)–C(6)	1.390(6)	1.356(3)	1.360
C(11)–C(12)	1.357(6)	1.347(3)	1.351
C(6)–C(7)	1.437(5)	1.454(3)	1.458
C(12)–C(1)	1.448(4)	1.458(3)	1.462
C(1)–C(13)	1.494(3)	1.503(2)	
C(7)–C(13)	1.485(4)	1.503(3)	
C(13)–F(1)	1.361(3)	1.370(2)	
C(13)–F(2)	1.365(3)	1.370(2)	

(b) Bond angles

	293 K	125 K †
C(13)–C(1)–C(2)	121.1(2)	121.3(2)
C(13)–C(7)–C(8)	120.2(3)	120.9(2)
C(13)–C(1)–C(12)	118.1(2)	118.2(2)
C(13)–C(7)–C(6)	118.2(3)	118.1(2)
C(12)–C(1)–C(2)	120.6(3)	120.3(2)
C(8)–C(7)–C(6)	121.4(3)	120.7(2)
C(1)–C(2)–C(3)	130.8(3)	130.2(2)
C(7)–C(8)–C(9)	132.0(4)	131.1(2)
C(2)–C(3)–C(4)	133.3(4)	130.7(2)
C(8)–C(9)–C(10)	133.2(5)	130.8(2)
C(3)–C(4)–C(5)	133.4(4)	132.8(2)
C(9)–C(10)–C(11)	132.3(4)	132.9(2)
C(4)–C(5)–C(6)	133.7(4)	134.8(2)
C(10)–C(11)–C(12)	135.0(4)	135.0(2)
C(5)–C(6)–C(7)	131.8(4)	132.4(2)
C(11)–C(12)–C(1)	132.0(3)	132.5(2)
C(1)–C(13)–C(7)	108.9(2)	109.2(2)
F(1)–C(13)–F(2)	102.6(2)	103.4(1)
C(1)–C(13)–F(1)	111.5(2)	111.4(1)
C(7)–C(13)–F(2)	111.8(2)	111.4(2)
C(1)–C(13)–F(2)	110.8(2)	110.7(1)
C(7)–C(13)–F(1)	111.1(2)	110.7(2)

* After rigid-body correction. † Rigid-body corrections to bond angles are $\leqslant 1\sigma$, and have been neglected.

Table 4. Torsion angles of 13,13-difluoro-1,7-methano[12]annulene compared with those of 4,10-dibromo-1,7-methano[12]annulene

	This work [a]		4,10-Dibromo derivative [b]
	293 K	125 K	(Room temp.)
C(12)–C(1)–C(2)–C(3)	−169.3	−173.4	−175.7
C(1)–C(2)–C(3)–C(4)	32.3	40.1	47.7
C(2)–C(3)–C(4)–C(5)	8.0	2.3	8.2
C(3)–C(4)–C(5)–C(6)	−18.7	−22.0	−41.3
C(4)–C(5)–C(6)–C(7)	−12.3	−4.1	−2.2
C(5)–C(6)–C(7)–C(8)	159.0	155.4	169.6
C(5)–C(6)–C(7)–C(13)	−15.7	−19.9	−6.1
C(13)–C(1)–C(2)–C(3)	5.3	1.8	−0.1

[a] Averaged assuming C_2 symmetry. E.s.d.s are in the range 0.4—1.2° at 293 K and 0.2—0.5° at 125 K. [b] This molecule has a crystallographic two-fold axis. E.s.d.s are *ca.* 0.4°.

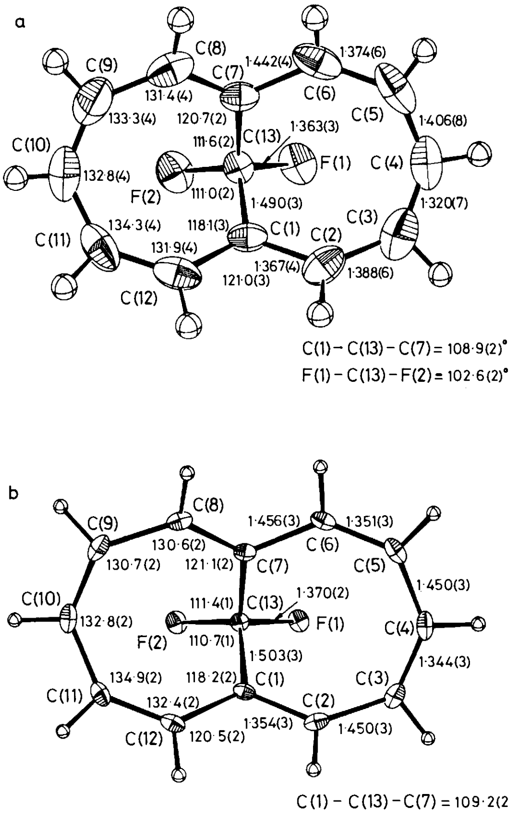

Figure 1. Numbering scheme, bond lengths, and bond angles of 13,13-difluoro-1,7-methano[12]annulene. Hydrogen atoms were numbered according to the carbon atom to which they are bonded. Thermal ellipsoids are drawn at 30% probability, but hydrogen atoms, treated as isotropic, are on an arbitrary scale. The values of the bond distances and angles are averages (assuming C_2 symmetry) of the individual values listed in Table 3. a, Room temperature (*ca.* 293 K); b, low temperature (*ca.* 125 K)

at room temperature are: F(1) $\cdots$ H(3)′ (at $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$) 2.78(3) Å, and F(2) $\cdots$ H(9)″ (at $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$) 2.76(3) Å. A quantity that gives an overall estimate of the tight or loose arrangement of molecules in a crystal is the Kitaïgorodski packing coefficient. For the present compound, we have calculated [13] values of 0.691 at 293 K and 0.726 at 125 K; we note for comparison that for this class of substances values of *ca.* 0.74 at room temperature are usually found for such a coefficient in close-packed crystals. Furthermore, the lack of strong packing interactions is reflected in the low potential energy barrier (<4 kcal mol^{-1}) [14] associated with a rotation as large as 20° around the axis of maximum inertia for the 125 K structure. All these findings indicate that at 293 K the molecules have an exceptionally high freedom in the crystal state, and support our suggested inadequacy of the usual model for atomic thermal motion at room temperature. No firm conclusions of chemical significance can therefore be drawn from the observation that at 293 K some ‘ long distances ’ appear to have the same value as some ‘ short distances ’: *e.g.* compare the ‘ long ’ C(2)–C(3) bond, 1.387(6) Å, with the ‘ short ’ C(5)–C(6) distance, 1.390(6) Å.

It is known that *X*-ray data alone cannot yield an accurate, quantitative description of bonding features in electron-density maps, unless high-order diffraction intensities are measured at very low temperature, and data are treated in a particularly accurate way. However, data of good quality,

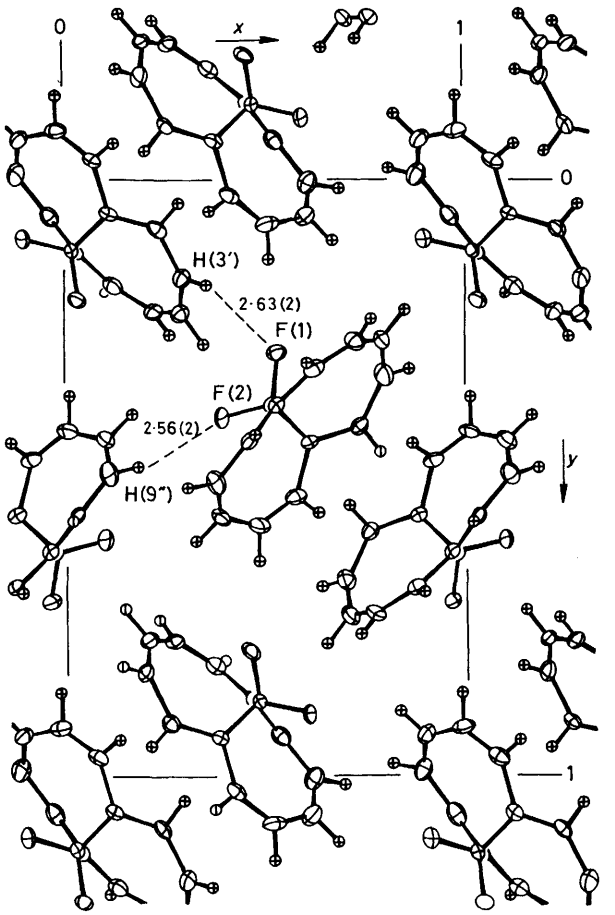

Figure 2. Low-temperature packing of the molecules as viewed along the *c* axis

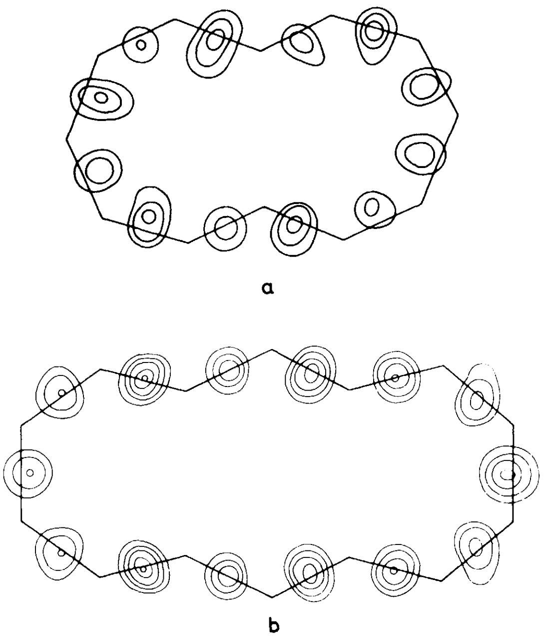

Figure 3. Sections of the ΔF synthesis showing residual electron density. In each composite, contour levels are at intervals of 0.05 e Å^{-3}; zero contours omitted. a, Title compound at 125 K; b, *anti*-1,6 : 8,13-bis(difluoromethano)[14]annulene at 200 K

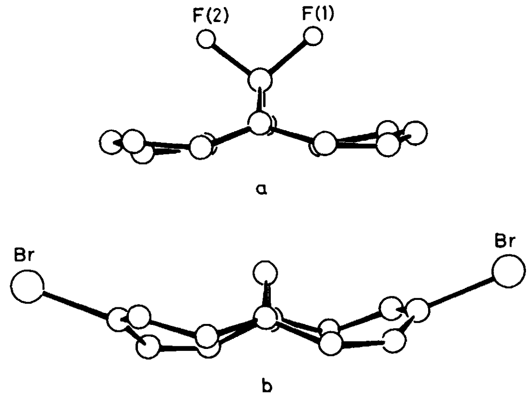

Figure 4. Side view of a, 13,13-difluoro-1,7-methano[12]annulene compared with that of b, 4,10-dibromo-1,7-methano[12]annulene, showing the different conformation of the [12]annulene ring in the two derivatives. Thermal ellipsoids have been replaced by spheres on an arbitary scale

collected at moderately low temperatures, can provide reliable qualitative information not accessible, for relatively large molecules, by approximate calculations. For the 125 K structure, we have calculated the deformation density, defined as the difference between the observed electron density and the electron density calculated for a superposition of spherical atoms, *i.e.*, $\rho_{def} = \rho_{obs} - \rho_{calc(sph)}$. The resulting maps have been collected in the composite of Figure 3a. It is seen that in accord with the large values of $\widehat{CCC}$ bond angles (all lying between 130 and 135°) the electron density of the C–C bonds is shifted inwards, substantiating the presence of the expected bent bonds. For comparison, in Figure 3b, a similar map is shown for a 14-membered cyclic polyene [namely *anti*-1,6 : 8,13-bis(difluoromethano)[14]annulene],[2] where the electron density shows no unusual features, and the bond angles are *ca.* 120°, except for the outer parts of the molecule, where $\widehat{CCC}$ values increase to *ca.* 125°, and the corresponding C–C bonds show inward bending.

One of the major points of interest of the present study is the comparison between the conformation of the 12-membered ring in the 13,13-difluoro-derivative (this work) and the 4,10-dibromo-compound.[4] It is readily apparent from a comparison of Figures 4a and b, and from the values of the torsion angles reported in Table 4, that the annulene ring shows two definitely different conformations in the two compounds. Empirical force field (EFF) calculations, performed as described in ref. 15 with some slight modifications, indicate that both conformations correspond to energy minima, whose difference amounts to 2.7 kcal mol^{-1}. This relatively low strain energy difference favours the conformation presented by the 4,10-dibromo-derivative, for which a detailed comparison between calculated and experimental geometries has been published.[15] The corresponding comparison for the 13,13-difluoro-compound, here studied, is reported in Figure 5: the agreement, as in the case of the other derivative, is more than satisfactory. The fact that two different conformations of the 1,7-methano-[12]annulene were found and calculated to be stable and lie very close in energy suggests that particular caution should be used in the interpretation of the n.m.r. data for this compound, due to the possible existence of an equilibrium of different conformers in solution.

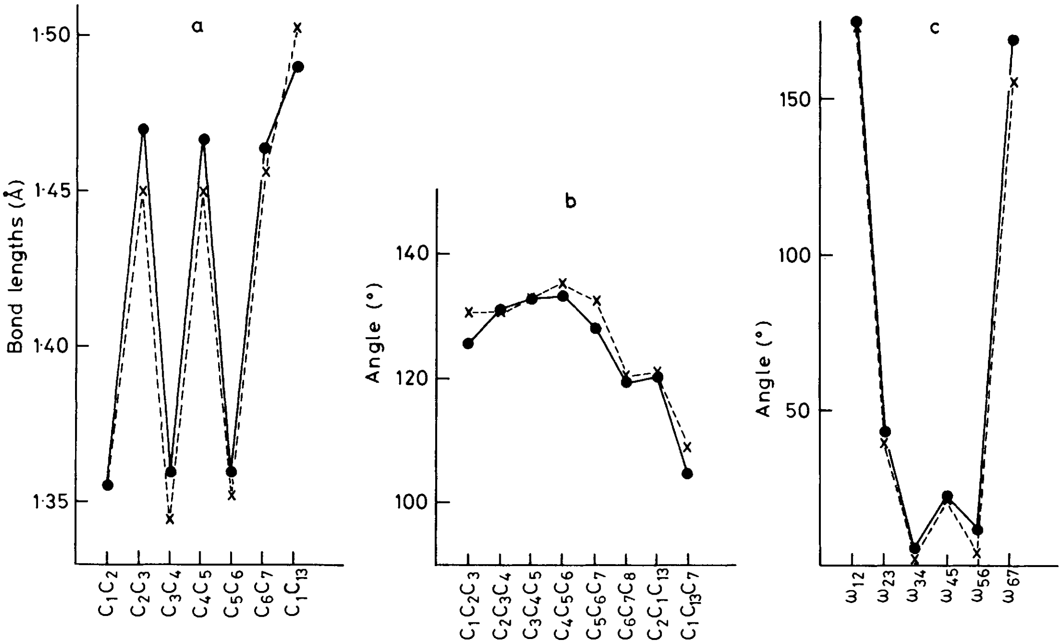

Figure 5. Comparison between experimental (×) and calculated (●) (by empirical force field method) bond distances, a; bond angles, b; and torsion angles, c

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