

precision of the structural results. The packing of the molecules is only slightly influenced by the disorder. All intermolecular contacts are normal. There is one type of short intermolecular halogen...halogen contact in each of the structures with lengths of 3.466 (1) Å for Cl(2)...Cl(3) in (I), 3.611 (1) Å for Br(2)...Br(2) in (II) and 3.756 (1) Å for I(1)...I(1) in (III). The contacts in (II) and (III), which are across centres of inversion, are indicated in the unit cells of Figs. 4, 5 and 6, and may be connected with very weak intermolecular bonding effects.

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What is the Favoured Conformation of the Friedelane Skeleton? A Combined X-ray and Molecular Force-Field Study of Friedelin, C₃₀H₅₀O

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Abstract

Friedelan-3-one, or friedelin has been studied both by X-ray and force-field methods in order to investigate a general conformational problem pertinent to the highly strained *cis*-fused rings *D* and *E* in the friedelane triterpenes. The crystals of friedelin, C₃₀H₅₀O, *M_r* = 426.73, m.p. 535–536 K, are orthorhombic, *P*2₁2₁2₁, *a* = 6.371 (1), *b* = 13.943 (2), *c* = 28.456 (5) Å, *V* = 2527.8 (7) Å³ at *T* = 293 (1) K, *Z* = 4, *D_x* = 1.121 Mg m⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 0.060 mm⁻¹, *F*(000) = 952. Diffractometer-data collected from a small crystal specimen contained a very large fraction of weak intensities. Structure solution was by direct methods. Least-squares refinement in the mixed temperature-factor mode was based on 2201 *F_o* and converged at *R* = 0.133. In the crystal structure the *D* ring is a deformed boat and the *E* ring is a boat,

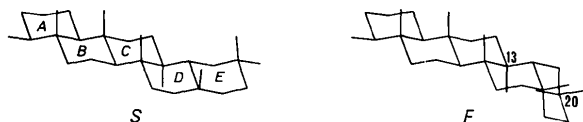
characterizing the stretched conformation. This has been found in eleven of fourteen crystalline derivatives of friedelane and closely related triterpenes. From ball-and-stick models it appears to be the favoured form. Force-field calculations of both the stretched and the folded (= *D* and *E* chairs) forms of the isolated friedelin molecule show that the two are very similar in energy, and the *folded* form is lower in energy by about 3.85 kJ mol⁻¹. One concludes that the conformational preference of a given derivative must be sensitive both to changes in substitution and in the crystalline environment. The calculations allow an analysis to be made of the individual contributions to strain in the two forms. Comparison with previous combined X-ray and force-field studies of similar systems suggests that in the present study of friedelin the calculated structure is more accurate than the experimental one. As part of this work, separate calculations for cyclohexanone have been carried out, and the results compared with those from other calculations and experiments.

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Introduction

The triterpene friedelin is found in nature primarily as a major constituent of cork. Its extremely low solubility in hydroxylic solvents has furthered suggestions that one of its functions may be to provide a hydrophobic coating for the protection of certain cells in the plant (Corey & Ursprung, 1956). Despite the efforts of several investigators following the initial extraction of cerin-friedelin mixtures from cork by Chevreul (1807), its constitution was not established until the work of Corey & Ursprung (1956), see also Brownlie, Spring, Stevenson & Strachan (1955).

Friedelin, or friedelan-3-one, is a prominent member of the friedelane group of triterpenes. An interesting conformational problem pertains to the highly strained *cis*-fused rings *D* and *E*. Masaki, Niwa & Kikuchi (1975) deduced from the inspection of Dreiding models eight possible conformations for *D* and *E*, provided rings *A* to *C* are retained in the chair form. According to these workers the energetically favoured forms are: (1) both rings *D* and *E* boat, which they called the stretched form (*S*), and (2) both *D* and *E* deformed chairs, called the folded form (*F*), with *S* more favoured than *F*. In a later study Laing and coworkers concluded that all molecules with the friedelane skeleton will be in the *S* form, because of the strong repulsion between the axial α -methyl groups at C(13) and C(20) in form *F* (Laing, Burke-Laing, Bartho & Weeks, 1977). Additional support for the view that *S* is the preferred form appeared in the work of Rogers, Phillips, Joshi & Viswanathan (1980).



Several derivatives of friedelane and related triterpenes have been studied by X-ray diffraction. Thus far the experimental evidence with respect to the conformation of rings *D* and *E* can be summed up as shown in Fig. 1: the stretched form is found in ten* structures, (Ia), (Ib), (IIa-d), (III), (IV), (V) and (VIII); three structures are in the folded form, (Ic), (VI) and (VII). Some of the stretched triterpenes, however, differ critically from the basic friedelane system in the rings *C-E*: (Ia), which has a large substituent at 16 β , (IIa) with a carbonyl function at C(12) which induces a flattening of ring *C*, and (V) with an oxide bridge across this ring. It was shown by Masaki *et al.* (1975), that a β -substituent at C(16) will favour the *S* conformation. In both (IIa) and (V), the chair form of ring *C* is distorted, apparently with the effect of moving the

* One additional example of the *S* form, inadvertently omitted from Fig. 1, is 4 β ,5 β -cyclofriedel-3-one (Connolly, Freer, Anjaneyulu, Ravi & Sambasivarao, 1986).

α -methyl group at C(13) closer to the one at C(20), thus destabilizing the *F* form. Among the folded structures, on the other hand, the conformation of (Ic) was deduced from a two-dimensional study, and could

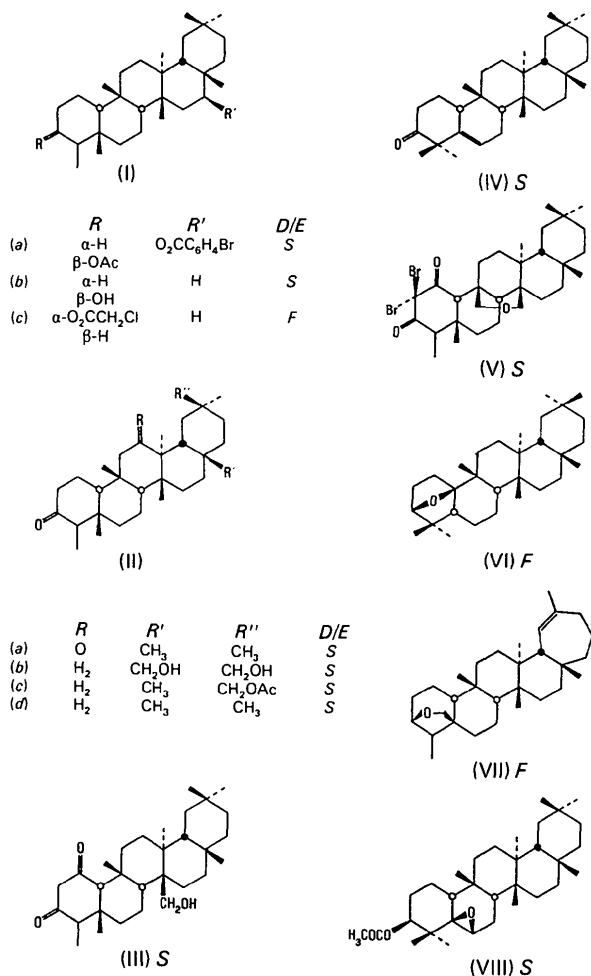


Fig. 1. Friedelanes and friedelane-like structures studied by X-ray diffraction. *S* and *F* denote stretched and folded forms, respectively. (Ia): 3 β -O-acetyl-16 β -O-(*p*-bromobenzoyl)pachysandiol B (Masaki, Niwa & Kikuchi, 1975); (Ib): friedelan-3 β -ol, or epifriedelinol (Laing, Burke-Laing, Bartho & Weeks, 1977); (Ic): friedelan-3 α -ol chloroacetate (Corey & Ursprung, 1956); (IIa): friedelan-3,12-dione, or prionostemmadione (Monache, Marini-Bettolo, Pomponi, de Mello, King & Thomson, 1979); (IIb): 17 β ,20 β -dihydroxymethylfriedelan-3-one, or maytenfoliol (Nozaki, Suzuki, Lee & McPhail, 1982); (IIc): 20 β -acetoxy-methylfriedelan-3-one (Betancor, Freire, Gonzalez, Salazar, Pascard & Prange, 1980); (II d): friedelan-3-one, or friedelin (present study); (III): 14 β -hydroxymethylfriedelan-1,3-dione (Rogers, Phillips, Joshi & Viswanathan, 1980); (IV): *D*:*B*-friedoolean-5-en-3-one, or alnusenone (Ohki, Tachibana, Kuroda, Takenaka & Sasada, 1981); (V): 2,2'-dibromo-25,26-epoxyfriedelan-1,3-dione (Rogers, Williams, Joshi, Kamat & Viswanathan, 1974); (VI): *D*:*B*-friedoolean-3 β ,10 β -epoxide, or campanulin (White, Fayos & Clardy, 1973; Mo, 1977); (VII): 3 β ,24-epoxy-20 α -homo-21-norfriedel-19-ene (Rogers, Woode, Viswanathan & Joshi, 1980); (VIII): *D*:*B*-friedoolean-5 β ,6 β -epoxy-3 β -yl acetate (Tori, Takai, Matsumoto, Moriyama, Tsuyuki, Takahashi, Itai & Iitaka, 1983).

be incorrect. Structure (VII) has a seven-membered ring E which is devoid of the *gem* dimethyl at C(20). This is important in considerations of strain in the folded form. In conclusion, despite the preponderance of the S form among the structures studied to date, the relative stabilities of the two conformations still seem to be in question.

Force-field (FF) calculations offer an alternative approach. Calculations of structure and energy have been carried out previously for campanulin (VI) (Mo, 1982). They showed form F to be slightly lower in energy than S , and the calculated geometry was in good agreement with the observations. It is of interest to examine whether the changes in rings A and B of friedelin (II*d*) compared with (VI) will influence the calculated relative stabilities of the two forms. In the present investigation of friedelin, therefore, we have combined X-ray and FF methods in an attempt to obtain a more reliable assessment of the conformational preference of the friedelane system.

Experimental

Crystals of friedelin, crystallized from chloroform, were kindly provided by the late Dr T. Bruun, Organic Chemistry Laboratories of this University. A prismatic specimen with dimensions $\sim 0.28 \times 0.23 \times 0.12$ mm was used for the analysis. The lattice parameters and crystal orientation were determined from the setting angles of 19 reflections in the 2θ range $26\text{--}38^\circ$. Measurements made at the beginning, at the end, and once during the data collection showed the maximum shift in any parameter to be about 1σ .

Reflections in two octants of reciprocal space, hkl and $h\bar{k}\bar{l}$, were measured without attenuators to $(\sin\theta)/\lambda = 0.65 \text{ \AA}^{-1}$ ($0 \leq h \leq 8$, $-16 \leq k \leq 18$, $-33 \leq l \leq 36$) with Nb-filtered Mo $K\alpha$ radiation on a Picker FACS-I diffractometer. The scan mode was $\omega/2\theta$ with basic ranges $2\theta(\alpha_1) - 0.5$ to $2\theta(\alpha_2) + 0.65^\circ$, backgrounds measured for 20 s at each end of the scan. Separate measurements of reflections with $2\theta < 9^\circ$ were made with scans reduced on the low-angle side to avoid or minimize effects of the Nb K absorption edge. Three standard reflections measured at intervals of 80 reflections showed variations of about $\pm 1\%$, and a steady decrease to about 93% of their initial values during the data collection. A normalized average standard curve was used for scaling the data. Data reduction included corrections for coincidence loss, which were generally small for this crystal because only three reflections had count rates in excess of 10 000 counts s^{-1} ; no absorption correction was applied. Two partial data sets comprising 2435 pairs of corrected F^2 were weight averaged and merged with 895 single measurements to yield a set of 3330 unique F^2 . Weights and standard deviations were calculated as given previously (Mo & Jensen, 1975); S in the relation

$\sigma^2(I) = \sigma_{\text{count}}^2 + (SI_{\text{net}})^2$ was adjusted to 0.025 to obtain a normal distribution of the weighted means of the differences $\Delta_i = (F_i^2 - F_{\text{ave}}^2)$ for all reflection pairs, $i = 1, 2$. The internal agreement index $D = \sum |F_i^2 - F_{\text{ave}}^2| / \sum F_{\text{ave}}^2 = 0.101$ for 1841 pairs with $F^2 > \sigma(F^2)$. In the final set of unique reflections, 1126, or nearly one-third, had $F^2 < \sigma(F^2)$, and were weighted zero. The remaining data with $w \neq 0$ had a very large fraction of weak reflections. Three reflections with $2\theta < 5^\circ$ were deleted.

The structure solution was not straightforward, and several unsuccessful attempts were made initially with two different tangent-refinement programs. A starting set comprising eight reflections finally yielded the correct solution. The program *TANNY* was applied in a stepwise manner, first developing and refining phases among the largest E 's before proceeding to smaller values (Mo, 1977). The program has no limit for the number of \sum_2 triples to be generated. From previous experience, we also deleted zonal reflections entering in the first cycles *via* single \sum_2 relations involving only reflections of the same zone. We ascribe the difficulties in solving the structure mainly to the many weak reflections in the data, and to the presence of pseudo-translational symmetry.

The E map for the best phase model, which included 307 terms > 1.6 , showed 30 of the 31 non-H atomic positions. The map also contained a set of weaker ghost maxima displaying pseudo-translational symmetry. These peaks were not present in subsequent ΔF maps. The R value for the 30-atom model was 0.36. In the initial refinement, the largest atomic shifts were applied from ΔF maps. Further refinement based on 2201 F_o was by blocked full-matrix least squares, minimizing the quantity $\sum w(|F_o| - k|F_c|)^2$ with weights $w = 1/\sigma^2(F_o)$. Isotropic and later anisotropic refinement of all C and O atoms converged at $R = 0.199$.

The positions of all H atoms were located with the aid of models in a ΔF map. Refinement in the mixed temperature-factor mode was checked frequently by ΔF maps. Near the end, the positions of 28 H atoms were fixed. Thermal parameters of the H atoms were physically reasonable, only three of the 50 U 's refined to values outside the range 0.01–0.15 \AA^2 . The refinement was terminated when average and maximum parameter shifts for the C and O atoms were 0.03 σ and 0.14 σ , respectively. The final R is 0.133, $wR = 0.060$ and the goodness of fit is 1.77. The residual density in the final difference map ranges from -0.50 to 0.53 e \AA^{-3} ; there are about ten peaks or troughs exceeding 0.4 e \AA^{-3} in magnitude.

Doyle & Turner's (1968) atomic form factors were used for C and O, and the values of Stewart, Davidson & Simpson (1965) were used for H. Standard crystallographic programs were from the *XRAY76* system (Stewart, 1976); the molecular drawings were prepared with *ORTEPII* (Johnson, 1976).

Table 1. *Calculated and experimental geometries of cyclohexanone*

Numbering of C atoms starts at the carbonyl end.

Bond lengths (Å)				C—C—C bond angles (°)				Torsion angles (°)			Puckering parameters (°)*		Dihedral angle (°)†	Method and reference
1=O	1-2	2-3	3-4	612	123	234	345	$\tau_{1,2}$	$\tau_{2,3}$	$\tau_{3,4}$	α	β	Δ_{eq}	
1.221	1.506	1.529	1.531	115.7	110.9	111.1	111.2	-51.5	52.8	-56.7	47.0	51.2	6.4	FFC ^a
1.222	1.506	1.537	1.539	116.4	110.3	110.8	111.3	-52.5	53.0	-57.0	47	51	5.6	FFC ^b
				115.9	111.8	112.2	112.1						5.8	FFC ^c
				115.7			111.2							CNDO/2 ^d
1.222‡	1.516‡	1.535‡	—	116.2‡	110.4	114.6	110.7							MW ^e

References (a) force-field calculation (this study), (b) force-field calculation (Krane, 1980), (c) force-field calculation (Fournier & Waegell, 1970), (d) CNDO/2 calculation (Fournier, 1975), (e) microwave spectroscopy, parameter set IV (Ohnishi & Kozima, 1968).

* Dihedral angles between planes (2356) and (612) (α) and (345) (β).

† Dihedral angle $OCCH_{eq}$.

‡ Assumed values.

Calculations

Calculations of structure and energy were based on a force field devised by Boyd (Chang, McNally, Shary-Tehrany, Hickey & Boyd, 1970; Boyd, 1975), but with some modifications introduced in the previous FF study of (VI) (Mo, 1982). Relevant to the present work are changes in the reference ('strain-free') values for C—C bond-stretch and C—C_{qt}—C angle-bend terms (C_{qt} denotes a quaternary C atom). We also retained a somewhat larger force constant, corresponding to an intrinsic torsional barrier of 11.1 kJ mol⁻¹ for the C(sp³)—C(sp³) bond. Calculation of torsional energy included all possible sequences X—C—C—Y, nine terms in all for each C(sp³)—C(sp³) bond.

For the carbonyl group in friedelin there appears to be no published FF parameters compatible with the Boyd field. This group is far removed from the rings involved in the conformational change, and therefore should be of minor significance. Nevertheless, we found it worthwhile for general purposes to start this part of the work by investigating and refining parameters for the carbonyl moiety through model calculations for different conformers of cyclohexanone.

Calculations for cyclohexanone

Krane (1980) has carried out calculations for some carbonyl compounds, and his structure results for the cyclohexanone chair are cited in the literature (Abraham, Bovill, Chadwick, Griffiths & Sancassan, 1980). We have adopted his parameters for the C(sp²)=O bond stretch. Our reference values for angle-bend terms involving C(sp²) and O are based on experimental results for acetone (Swalen & Costain, 1959; Nelson & Pierce, 1965) and cyclohexanone (Ohnishi & Kozima, 1968), and CNDO calculations for cyclohexanone (Fournier, 1975). Corresponding force constants were those obtained by scaling against the parameters of Allinger (Allinger, Tribble, Miller & Wertz, 1971; Allinger, Tribble & Miller, 1972) and Ermer & Lifson (1973).

Several different schemes were tested for describing torsion about a C(sp³)—C(sp²)O bond. They include a

sum of one-, two- and threefold potentials as used by Krane (1980), or threefold only, in either case with or without an out-of-plane term for the [C(sp³)]₂—C(sp²)=O group. We found a single threefold potential including an out-of-plane term adequate. The force constant employed corresponds to the rotational barrier of acetone (Swalen & Costain, 1959). Following Fournier & Waegell (1970) only terms X—C(sp³)—C(sp²)—C(sp³) with X = C, H were considered, which gives three terms per bond; the potential for the terms X—C(sp³)—C(sp²)=O was set equal to zero.

Finally, non-bonded potential curves involving C(sp²) and O were obtained by scaling against the curve for C(sp³) prepared from the values of Boyd

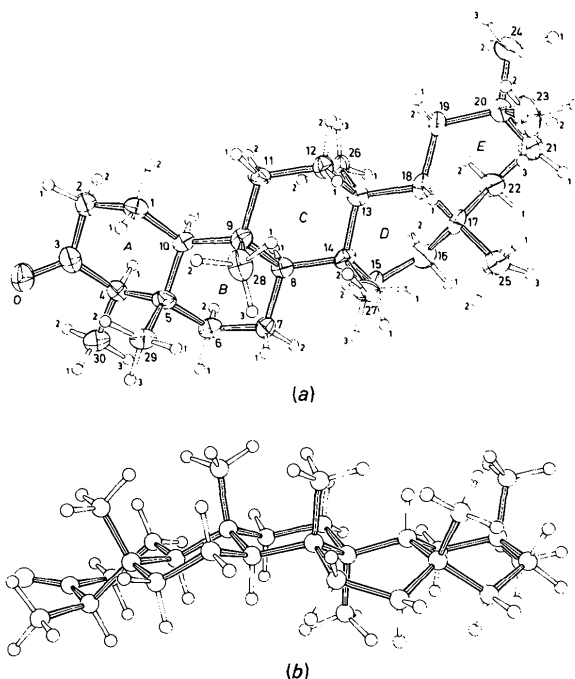


Fig. 2. (a) Molecular conformation of friedelin with thermal ellipsoids for the C and O atoms. Numbering of H atoms gives only the sequence at each attached C. (b) View of the molecule showing the conformation of the rings.

Table 2. Atomic parameters of experimental and calculated structures

X-ray structure: coordinates (x, y, z) in fractions of cell edges are $\times 10^4$ for C and O, and $\times 10^3$ for H. Thermal parameters, U_{eq} ($\text{\AA}^2 \times 10^4$) for C and O, are calculated from $U_{eq} = \frac{1}{3} \sum_i U_{ij} a_i^* a_j^* a_i a_j$ with U_{ij} defined by: $T(\theta) = \exp[-2\pi^2(U_{11}a^{*2}h^2 + \dots + 2U_{12}a^*b^*hk + \dots)]$ and U_{iso} ($\text{\AA}^2 \times 10^3$) for H is defined by: $T(\theta) = \exp[-8\pi^2U(\sin^2\theta/\lambda^2)]$. E.s.d.'s are given in parentheses.

Force-field structure: coordinates (X, Y, Z) in orthogonal Angstrom space are given in italics.

	x	y	z	U_{eq}	X	Y	Z		x	y	z	U_{iso}	X	Y	Z
O	859 (7)	2123 (3)	5126 (1)	586 (31)	0.37701	2.99647	14.58599	H(72)	154 (5)	-68 (2)	320 (1)	5 (11)	0.99743	-1.00926	9.00843
C(1)	2208 (10)	2771 (4)	4003 (2)	426 (41)	1.43670	3.86850	11.38750	H(81)	52 (6)	92 (2)	302 (1)	11 (11)	0.20095	1.29406	8.58861
C(2)	671 (11)	2970 (4)	4401 (2)	484 (45)	0.42689	4.14570	12.49900	H(101)	14 (9)	193 (4)	361 (2)	39 (14)	0.05930	2.72110	10.29835
C(3)	466 (10)	2104 (5)	4702 (2)	468 (45)	0.25048	2.93642	13.37290	H(111)	340 (6)	318 (2)	304 (1)	18 (12)	2.25775	4.42928	8.75366
C(4)	-91 (11)	1184 (4)	4457 (2)	409 (42)	-0.07378	1.65229	12.64928	H(112)	116 (7)	277 (3)	298 (1)	42 (14)	0.63518	3.89575	8.41864
C(5)	1634 (10)	964 (4)	4077 (2)	379 (41)	1.01797	1.34062	11.59098	H(121)	500 (7)	233 (3)	243 (1)	45 (14)	3.14782	3.21973	6.82401
C(6)	918 (11)	74 (4)	3786 (2)	464 (43)	0.60658	0.08195	10.80109	H(122)	290 (9)	298 (4)	223 (2)	62 (16)	1.84655	4.26700	6.36712
C(7)	2163 (10)	-85 (4)	3340 (2)	378 (39)	1.39752	-0.12783	9.50871	H(151)	222 (7)	-84 (3)	237 (1)	45 (14)	1.39530	-1.23508	6.69870
C(8)	2059 (9)	801 (4)	3018 (2)	317 (37)	1.27236	1.11041	8.60590	H(152)	6 (8)	-23 (3)	252 (1)	47 (13)	-0.08690	-0.43004	7.11678
C(9)	2956 (10)	1711 (4)	3266 (2)	353 (40)	1.88768	2.36263	9.30060	H(161)	55 (8)	-75 (4)	158 (2)	90 (19)	0.34634	-1.25024	4.66909
C(10)	1703 (10)	1840 (4)	3727 (2)	373 (40)	1.08891	2.57046	10.62805	H(162)	-64 (11)	9 (5)	173 (2)	69 (17)	-0.59710	0.13908	5.00293
C(11)	2699 (10)	2577 (4)	2949 (2)	373 (39)	1.67886	3.58358	8.38010	H(181)	466 (9)	139 (4)	175 (2)	50 (15)	2.89355	1.90126	4.82685
C(12)	3415 (9)	2417 (4)	2443 (2)	375 (40)	2.07081	3.35005	6.91109	H(191)	376 (6)	286 (3)	154 (1)	27 (12)	1.98452	4.05551	4.29528
C(13)	2294 (10)	1559 (4)	2202 (2)	318 (39)	1.33283	2.15771	6.26485	H(192)	127 (9)	241 (4)	130 (2)	34 (13)	0.42154	3.37446	3.94263
C(14)	2713 (9)	637 (4)	2496 (2)	379 (42)	1.64590	0.87836	7.10736	H(211)	394 (12)	81 (5)	56 (2)	73 (17)	2.16990	1.10919	1.46201
C(15)	1375 (10)	-195 (4)	2278 (2)	426 (43)	0.83349	-0.31289	6.54283	H(212)	215 (7)	146 (3)	37 (2)	71 (18)	0.70976	1.91155	0.96649
C(16)	992 (12)	-124 (5)	1746 (2)	614 (51)	0.42260	-0.23450	5.06182	H(221)	81 (12)	6 (5)	85 (2)	52 (15)	0.21530	-0.03814	2.38645
C(17)	2528 (11)	472 (4)	1441 (2)	435 (44)	1.33124	0.59927	4.13764	H(222)	25 (11)	105 (5)	101 (2)	95 (20)	-0.37678	1.43902	3.09653
C(18)	3258 (9)	1421 (4)	1695 (2)	317 (37)	1.80641	1.94351	4.78914	H(231)	656 (10)	215 (5)	51 (2)	156 (25)	3.67490	3.04396	1.19335
C(19)	2881 (10)	2319 (4)	1392 (2)	460 (46)	1.48989	3.17018	3.89780	H(232)	637 (12)	284 (6)	101 (2)	106 (20)	3.77426	4.07372	2.62082
C(20)	3632 (12)	2236 (5)	862 (2)	527 (51)	1.87474	3.03343	2.41482	H(233)	654 (12)	156 (5)	102 (2)	69 (17)	3.90954	2.32787	2.78621
C(21)	2804 (13)	1314 (5)	645 (2)	683 (56)	1.34110	1.71214	1.83385	H(241)	374 (8)	312 (3)	32 (2)	80 (18)	1.52008	4.16775	0.59125
C(22)	1390 (12)	723 (5)	987 (2)	567 (48)	0.53684	0.89589	2.85109	H(242)	125 (11)	303 (5)	58 (2)	144 (24)	0.16067	4.18177	1.71770
C(23)	6093 (14)	2258 (7)	862 (2)	901 (69)	3.39794	3.12147	2.24544	H(243)	323 (9)	375 (4)	74 (2)	100 (22)	1.59170	5.15977	2.04819
C(24)	2843 (12)	3121 (5)	606 (2)	688 (53)	1.24901	4.20509	1.64719	H(251)	575 (11)	22 (4)	123 (2)	71 (17)	3.34211	0.25904	3.31735
C(25)	4410 (12)	-177 (5)	1313 (2)	662 (52)	2.51214	-0.30772	3.73430	H(252)	485 (9)	-62 (4)	160 (2)	95 (20)	2.88274	-0.89546	4.57033
C(26)	8 (10)	1822 (4)	2172 (2)	402 (41)	-0.16968	2.54720	6.27728	H(253)	423 (10)	-65 (4)	104 (2)	98 (20)	2.19895	-1.03069	2.98044
C(27)	5049 (11)	328 (4)	2480 (2)	460 (40)	3.13765	0.47905	7.03120	H(261)	-74 (7)	155 (3)	187 (1)	31 (13)	-0.76890	1.94357	5.60638
C(28)	5415 (9)	1628 (4)	3377 (2)	457 (43)	3.40591	2.26486	9.57422	H(262)	-75 (6)	178 (3)	249 (1)	46 (14)	-0.61933	2.47160	7.26290
C(29)	3705 (12)	751 (5)	4321 (2)	525 (48)	2.34731	1.06243	12.32130	H(263)	-9 (11)	255 (5)	209 (2)	94 (21)	-0.30347	3.58184	5.96251
C(30)	-579 (12)	381 (4)	4813 (2)	608 (47)	-0.35237	0.52554	13.65521	H(271)	540 (11)	-1 (5)	222 (2)	112 (21)	3.45152	0.24074	6.02450
								H(272)	609 (11)	92 (5)	252 (2)	104 (21)	3.79832	1.26995	7.36145
								H(273)	515 (11)	-3 (5)	275 (2)	98 (20)	3.34244	-0.39914	7.64245
				U_{iso}				H(281)	606 (10)	193 (4)	314 (2)	79 (18)	3.98938	2.70410	8.76853
H(11)	367 (8)	277 (4)	408 (2)	68 (17)	2.43197	3.80643	11.82387	H(282)	577 (11)	198 (5)	363 (2)	91 (20)	3.68615	2.82317	10.46408
H(12)	218 (6)	327 (3)	375 (1)	29 (13)	1.44055	4.72441	10.71379	H(283)	595 (11)	95 (4)	344 (2)	93 (19)	3.74661	1.24105	9.69962
H(21)	98 (8)	356 (3)	456 (2)	66 (16)	0.75670	4.98696	13.11116	H(291)	456 (11)	42 (4)	410 (2)	68 (18)	3.15611	0.84255	11.63337
H(22)	-75 (9)	300 (4)	423 (2)	105 (21)	-0.54504	4.40208	12.07442	H(292)	474 (9)	132 (3)	443 (2)	95 (21)	2.64717	1.90568	12.94187
H(41)	-136 (12)	131 (4)	423 (2)	56 (16)	-1.01161	1.82460	12.11718	H(293)	365 (12)	28 (5)	463 (2)	109 (22)	2.25812	0.19418	12.97244
H(61)	85 (9)	-54 (3)	401 (2)	91 (19)	0.71663	-0.80558	11.42545	H(301)	75 (12)	19 (4)	490 (2)	150	0.51712	0.32071	14.27892
H(62)	-81 (9)	14 (3)	374 (2)	23 (12)	-0.45220	0.15054	10.54503	H(302)	-174 (11)	62 (5)	505 (2)	108 (21)	-1.17265	0.80879	14.31603
H(71)	376 (11)	-28 (4)	339 (2)	99 (20)	2.43642	-0.35425	9.73787	H(303)	-98 (11)	-19 (4)	467 (2)	66 (17)	-0.64506	-0.39509	13.15160

(Chang *et al.*, 1970). Our complete force field has been deposited.* All calculations of structure and energy were carried out with a locally modified version of the program *MOLBD2* (Boyd, 1968; Boyd, Breitling & Mansfield, 1973).

The geometry obtained for cyclohexanone (chair) is given in Table 1 along with results from other calculated and experimental geometries for this molecule.

Calculations for friedelin

Both forms were investigated. Starting parameters for the C and O atoms of the *S* form were taken from the crystallographic study at $R = 0.155$. A model of the

* Lists of parameters for the force-field calculations, structure factors, anisotropic displacement parameters and short intramolecular contacts for the *S* form, and atomic coordinates for the *F* form from the FF calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51534 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

F form was obtained by fitting together X-ray coordinates for the C and O atoms of rings *A*, *B* and *C* of friedelin and rings *C*, *D* and *E* of campanulin (VI). In both models H-atom coordinates were assigned according to idealized geometries. An 8.5 Å cut-off was used for the nonbonded interactions.

Potential energies were minimized until the final r.m.s. shifts of the coordinates were 0.00045 Å for *F* and 0.00090 Å for *S*. The final energies differ by 3.85 kJ mol⁻¹, with *F* lower than *S*.

Results and discussion

Friedelin crystallizes in the stretched (*S*) conformation as shown in Fig. 2. The C and O atoms are labelled according to the system used previously for (VI) (Mo, 1977). Table 2 gives atomic coordinates and thermal parameters from the crystallographic refinement together with the calculated coordinates for the *S* form.

The least-squares refinement converged at $R = 0.133$ with relatively large e.s.d.'s in the parameters. We believe that the main reason for this and for the rather high value of the agreement index *D* is the large fraction

Table 3. Observed and calculated endocyclic torsion angles ($^{\circ}$)

Values from the calculations are given in italics.

Ring A				Ring B				Ring C			
	Obs.	Calc.	$\Delta^* \times 10$		Obs.	Calc.	$\Delta \times 10$		Obs.	Calc.	$\Delta \times 10$
1,2	+51.4 (3)	+51.3	-1	5,6	+51.1 (5)	+48.1	-30	8,9	+46.8 (7)	+48.0	+12
2,3	-53.6 (5)	-52.4	-12	6,7	-57.6 (5)	-56.4	-12	9,11	-47.8 (6)	-47.9	+1
3,4	+58.5 (6)	+56.5	-20	7,8	+59.6 (6)	+62.6	+30	11,12	+56.5 (6)	+56.6	+1
4,5	-58.4 (6)	-57.2	-12	8,9	-56.2 (6)	-59.9	+37	12,13	-58.1 (5)	-58.0	-1
5,10	+58.6 (6)	+59.3	+7	9,10	+55.0 (6)	+54.4	-6	13,14	+54.2 (6)	+55.1	+9
10,1	-56.4 (4)	-57.2	+8	10,5	-51.8 (6)	-48.7	-31	14,8	-51.5 (7)	-53.7	+22

Ring D			Ring E			Ring					
	Obs.	Calc.		Obs.	Calc.		$\bar{\Delta}^*$	$\overline{ \Delta }$	r^\dagger		
13,14	-67.9 (6)	-63.3	-46	17,18	-7.1 (7)	-6.2	-9	A	-0.50	1.00	1.16
14,15	+30.6 (7)	+25.3	-53	18,19	-47.1 (7)	-47.4	+3	B	-0.20	2.43	2.68
15,16	+23.0 (8)	+27.3	+43	19,20	+49.5 (7)	+49.7	+2	C	+0.73	0.77	1.09
16,17	-39.0 (8)	-41.8	+28	20,21	+2.2 (6)	+1.7	-5	D	-0.60	3.73	3.88
17,18	+0.4 (7)	+2.7	+23	21,22	-57.1 (6)	-55.7	-14	E	-0.63	0.80	0.95
18,13	+52.5 (6)	+49.4	-31	22,17	+58.7 (6)	+57.2	-15	A,C,E	-0.13	0.86	1.07
								B,D	-0.40	3.08	3.34

$$* \Delta = (|\text{calc.}| - |\text{obs.}|)$$

$$\dagger r = [(1/n) \sum_{i=1}^n \Delta_i^2]^{1/2}$$

of weak reflections above the $1\sigma(F^2)$ threshold. However, both the distribution of the weighted Δ_i 's from the data averaging and the final value of $wR = 0.060$ indicate that the data are of better quality than might be inferred from the unweighted R alone. Nevertheless, the present structure study can be taken to represent a case in which the diffraction data are impaired by the quality of the crystal, or its size or both. Calculations of structure may then offer a preferable alternative. It is essential, therefore, to establish from crystallographic criteria (R indices, e.s.d.'s in parameters, goodness of fit, etc.) the cases for which calculations at a given level of sophistication are likely to give a more reliable geometry than does the diffraction experiment. This requires detailed comparisons to be made, on the one hand between calculated and experimental models of the same structure, on the other hand between different experimental models of the same structure, or between structures having a large fragment in common.

For (VI), the other triterpene studied by FF methods, the crystallographic structure had e.s.d.'s 0.003–0.004 Å in bond lengths and $\sim 0.2^\circ$ in bond angles, the final R based on $2290 F_o$ was 0.039 (Mo, 1977). Comparison of this model with a common fragment of the closely related baccharis oxide structure provided a measure of the experimental accuracy. The results showed that for (VI), the FF calculations were inferior to the experimental structure (Mo, 1982).

In the present case, however, there is good evidence (see *Bond lengths and angles*) that the calculated structure is the more reliable.

Molecular conformation

Table 3 gives the endocyclic torsion angles. Rings A, B and C are chairs; for A and C calculated and observed values compare well. The calculations give a stronger flattening, $\sim 3^\circ$, about the bonds to C(5) in

ring B, and correspondingly more pucker at C(8). The observed flattening of ring C is reproduced in good detail by the calculations.

According to Masaki *et al.* (1975) the D and E rings are boats in the S conformation. Ring D in friedelin departs markedly from this form, observed torsion angles being $\sim 31^\circ$ about C(14)–C(15) and $\sim 23^\circ$ about C(15)–C(16), compared with ~ 0 and $\sim 54^\circ$, respectively, for a boat. The effect of the distortion, which is primarily a bending away of C(16) from the α -side of the molecule, is to relieve the strong repulsion between H(162) and the axial C(26)H₃ methyl group. In the resulting structural compromise the distance H(162)···H(261) is 1.91 Å (calculated), but the H atoms on C(15) and C(16) have been forced into more eclipsed positions (Fig. 2b) and both these neighbouring H···H distances are < 2.30 Å. Ring E is a boat, X-ray and FF parameters are in very good agreement.

Ring D has the largest r.m.s. deviation between experimental and calculated torsion angles, $\sim 3.9^\circ$. Intermolecular contacts involving methyl groups 25, 26 and 27 could contribute to the differences which range up to about 5° . It is interesting, however, that our experimental values are in fair agreement with those for structures (Ib) (Laing *et al.*, 1977) and (IV) (Ohki, Tachibana, Kuroda, Takenaka & Sasada, 1981). The r.m.s. and maximum deviations between the D rings in friedelin and (Ib) are 1.7 and 3.6° , respectively. The corresponding figures for structure (IV) are 2.4 and 4.4° .

The molecular conformation is determined mainly by the axial methyl groups. Diaxial C···C contacts C(25)···C(27)···C(28)···C(29) are in sequence: 3.42 (3.45), 3.14 (3.12) and 3.15 (3.18) Å (calculated distances in parentheses). There are several C(Me)···H distances shorter than a normal van der Waals contact; a list of short intramolecular contacts has been deposited. Of the 30 H···H intramolecular distances

Table 4. Observed and calculated bond lengths (Å)

Values from the calculations are given in italics.

	Obs.	Calc.	$\Delta^* \times 10^3$		Obs.	Calc.	$\Delta^* \times 10^3$
0-3	1.234 (7)	1.221	-13	15-16	1.536 (8)	1.539	3
1-2	1.522 (9)	1.527	5	16-17	1.550 (9)	1.541	-9
2-3	1.487 (9)	1.502	15	17-18	1.578 (9)	1.568	-10
3-4	1.501 (9)	1.509	8	18-13	1.580 (8)	1.565	-15
4-5	1.572 (9)	1.552	-20	18-19	1.538 (8)	1.549	11
5-10	1.577 (8)	1.564	-13	19-20	1.586 (8)	1.538	-48
10-1	1.550 (8)	1.544	-6	20-21	1.521 (10)	1.539	18
5-6	1.560 (8)	1.542	-18	21-22	1.561 (10)	1.532	-29
6-7	1.513 (8)	1.530	17	22-17	1.522 (9)	1.541	19
7-8	1.539 (8)	1.538	-1	20-23	1.568 (12)	1.535	-33
8-9	1.561 (8)	1.559	-2	20-24	1.520 (10)	1.534	14
9-10	1.546 (9)	1.563	17	17-25	1.546 (10)	1.543	-3
9-11	1.516 (8)	1.543	27	13-26	1.505 (9)	1.552	47
11-12	1.528 (8)	1.538	10	14-27	1.551 (9)	1.546	-5
12-13	1.554 (8)	1.544	-10	9-28	1.602 (9)	1.546	-56
13-14	1.556 (8)	1.564	8	5-29	1.521 (9)	1.542	21
14-8	1.558 (9)	1.562	4	4-30	1.541 (8)	1.536	-5
14-15	1.568 (9)	1.548	-20				

All 35 bonds $\bar{\Delta}$ -0.0021 $\overline{|\Delta|}$ 0.0160 r^\dagger 0.0206

* Δ = (calc. - obs.).
 $\dagger r = [(1/n)\sum_{i=1}^n \Delta_i^2]^{1/2}$.

calculated ≤ 2.30 Å, 19 involve H in axial methyl groups. The C(25)H₃ and C(27)H₃ methyl groups, together with H(181), form a closed loop of short H...H contacts; H(271)...H(252) in this loop is only 1.93 Å according to the calculations. The contact H(281)...H(272) is a common link in two similar loops, H(121) participates in one of them, and H(71) in the other. Methyl C(28)H₃ also forms short contacts with H(11) and H(291). On the opposite side of the molecule the C(26)H₃ group is locked rigidly. Its H atoms are involved in five H...H contacts calculated to be < 2.30 Å, among them are H(261)...H(162), 1.91 and H(262)...H(81), 1.95 Å.

Bond lengths and angles

These parameters are given in Tables 4 and 5. The general trend in experimental bond lengths within the ring structure is reproduced reasonably well by the calculations. Nine bonds involving quaternary C atoms were calculated to be > 1.55 Å. With one exception, they are also long in the X-ray model. The exception, C(13)-C(26) has a $\Delta = 0.047$ Å, and Table 4 reveals some other glaring discrepancies as well. For the bonds with the largest Δ 's, which involve some of the methyl groups and the three bonds in the sequence 19-22, there appears to be systematic errors in the observed values. Of the 35 bonds in Table 4, nine deviate from the calculated lengths by 0.020 Å or more, the r.m.s. difference for all bonds being 0.021 Å. In the study of (VI) only one bond-length difference exceeded 0.020 Å, and the r.m.s. difference was 0.009 Å.

The Δ 's in bond angles are generally smaller than might be expected from the results for the bonds. The r.m.s. difference for all 62 pairs in Table 5, 1.20°, may be compared with the 1.11° obtained for (VI). Seven

Table 5. Observed and calculated valency angles (°)

Values from the calculations are given in italics.

	Obs.	Calc.	$\Delta^* \times 10$		Obs.	Calc.	$\Delta^* \times 10$
2-1-10	113.3 (5)	111.2	-21	12-13-18	108.5 (5)	110.8	23
1-2-3	109.7 (5)	110.8	11	12-13-26	106.3 (5)	105.4	-9
2-3-4	116.6 (5)	115.5	-11	14-13-18	109.0 (5)	109.6	6
0-3-2	121.9 (6)	121.7	-2	14-13-26	113.4 (5)	113.3	-1
0-3-4	121.3 (6)	122.7	14	18-13-26	110.8 (5)	109.6	-12
3-4-5	108.7 (5)	110.3	16	8-14-13	110.2 (5)	110.3	1
3-4-30	111.4 (5)	110.4	-10	8-14-15	109.9 (5)	109.8	-1
5-4-30	116.8 (5)	115.3	-15	8-14-27	109.0 (5)	108.4	-6
4-5-6	108.5 (5)	109.0	5	13-14-15	107.7 (5)	109.1	14
4-5-10	107.6 (5)	107.1	-5	13-14-27	112.2 (5)	112.2	0
4-5-29	109.2 (5)	108.6	-6	15-14-27	107.7 (5)	106.8	-9
6-5-10	106.8 (5)	109.8	30	14-15-16	115.4 (5)	116.9	15
6-5-29	110.0 (5)	109.0	-10	15-16-17	119.1 (6)	116.6	-25
10-5-29	114.6 (5)	113.2	-14	16-17-18	112.3 (5)	113.2	9
5-6-7	114.2 (5)	114.0	-2	16-17-22	107.3 (6)	107.5	2
6-7-8	111.1 (5)	110.1	-10	16-17-25	107.9 (5)	106.9	-10
7-8-9	111.5 (5)	110.7	-8	18-17-22	109.7 (5)	109.8	1
7-8-14	116.0 (5)	115.1	-9	18-17-25	111.8 (5)	112.4	6
9-8-14	116.9 (5)	116.9	0	22-17-25	107.7 (5)	106.8	-9
8-9-10	106.9 (5)	106.5	-4	13-18-17	113.9 (5)	114.7	8
8-9-11	109.8 (5)	108.4	-14	13-18-19	110.6 (5)	111.9	13
8-9-28	112.9 (5)	114.6	17	17-18-19	112.3 (5)	112.2	-1
10-9-11	110.8 (5)	109.4	-14	18-19-20	115.2 (5)	115.7	5
10-9-28	110.3 (5)	111.1	8	19-20-21	110.1 (5)	110.7	6
11-9-28	106.3 (5)	106.8	5	19-20-23	107.5 (5)	110.5	30
1-10-5	109.6 (5)	111.6	20	19-20-24	107.3 (5)	108.2	9
1-10-9	114.9 (5)	114.5	-4	21-20-23	111.3 (6)	110.6	-7
5-10-9	117.3 (5)	116.2	-11	21-20-24	112.1 (6)	109.0	-31
9-11-12	114.3 (5)	114.5	2	23-20-24	108.3 (6)	107.8	-5
11-12-13	113.1 (5)	113.3	2	20-21-22	113.1 (5)	112.9	-2
12-13-14	108.6 (5)	108.1	-5	17-22-21	112.1 (6)	112.7	6

All 62 angles $\bar{\Delta}$ -0.03 $\overline{|\Delta|}$ 0.95 r 1.20

* Δ = (calc. - obs.).
 $\dagger r = [(1/n)\sum_{i=1}^n \Delta_i^2]^{1/2}$.

angles in friedelin have $\Delta \geq 2.0^\circ$ compared with four in (VI). It should be noted, however, that the angular range (H excluded) in the latter structure is very large, 98.9-122.2° (X-ray) and will be more difficult to reproduce in calculations. In friedelin the corresponding range is 106.3-119.1°.

We have compared the calculated bond lengths and angles of rings C, D and E in friedelin with those observed in structure (IV), which has the same conformation for the three rings. The e.s.d.'s in the crystallographic parameters of (IV) are significantly smaller than in friedelin, 0.003-0.005 Å in bonds, 0.2-0.4° in angles (Ohki *et al.*, 1981). The comparison reveals an excellent agreement between calculated and experimental values for the 22 C-C bonds in the common molecular fragment which includes atom C(28); the average ($\overline{|\Delta|}$) and r.m.s. (r) differences are 0.0045 and 0.0063 Å, respectively. For the 38 C-C angles involved, $\overline{|\Delta|} = 0.68$ and $r = 0.89^\circ$. From all these observations we conclude, therefore, that until a better experimental model for friedelin is available, the *calculated* set of bond lengths and angles should be regarded as the more reliable.

The X-ray structure parameters involving H are largely of diagnostic value. For about half of the H atoms, the coordinates had to be fixed at the end of the refinement, the final C-H distances ranging from 0.86 to 1.12 Å.

Molecular packing

All methyl groups participate in intermolecular contacts; of the methylene groups, C(1)H₂ and C(2)H₂ contribute in particular. The shortest C...H and H...H contacts, C(24)...H(303)^{4,*} 2.75 and H(21)...H(302)³, 2.15 Å, are within normal ranges. The carbonyl groups of adjacent molecules along *c* are stacked in antiparallel arrays (see Fig. 3) with contact distances O...C(3)³, 3.17(1) Å. This arrangement, which indicates a certain amount of dipolar interaction, has been observed in other crystal structures, see Jeffrey, Rosenstein & Vlasse (1967).

The molecular packing is different in the crystals of friedelin and (VI), but common to both are relatively weak intermolecular forces and a coordination number of 10.

Comparison of the calculated structures

According to our FF calculations, the *F* form of friedelin is slightly more stable than *S*. This is in contrast to the conformation observed in the crystal and, in particular, to the conclusion based on ball-and-stick models of the friedelane system. It is of interest to analyse this result in some detail to rationalize the apparent anomaly.

The results of the FF calculations are summarized in Table 6. Before discussing the numbers, we recall the following points:

(1) A necessary requirement of a force field is that it should give a calculated structure in good agreement with the observed one. The experimental model of friedelin is too inaccurate to serve as a test. However,

Table 6. Calculations of strain energy (kJ mol⁻¹)

Energy term	<i>F</i>	<i>S</i>	$\Delta(F-S)$
Bond stretch	32.284	31.497	0.787
Angle bend	74.550	57.145	17.405
Torsion	38.874	59.260	-20.386
Out-of-plane bend	0.008	0.008	0
Nonbonded	120.973	122.627	-1.654
Total	266.689	270.537	-3.848

comparison with a large fragment of structure (IV), and previous calculations for (VI) indicate that the force field employed here has good properties for this type of molecule.

(2) The present calculations consider a single molecule. Thus, the contributions from *intermolecular* interactions are neglected in the nonbonded energy term. These interactions will influence mainly the torsion angles. Depending on the molecular flexibility, a change in the crystalline environment may favour a different conformer.

(3) FF methods are approximate, and the inherent deficiencies of a given potential will affect the numerical values for the calculated energies. However, energy *differences* between conformers usually are significant and consistent.

For both conformers the largest term is the (intra-molecular) nonbonded energy. In the *S* form several C...C contacts contribute, the ones highest in energy are the bow-stern contacts in rings *C* and *D*, 19...22, 2.68 and 13...16, 2.83 Å. They alone represent 13.48 kJ mol⁻¹, or about 11% of the total nonbonded energy. All H...H contacts ≤ 2.30 Å contribute significantly, the energy associated with the eight shortest ones, < 2.10 Å, amounts to about 28% (34.92 kJ mol⁻¹) of the nonbonded total. In form *F* the shortest C...C contact is 3...10, 2.90 Å, which is present also in the *S* form. There are 30 H...H distances ≤ 2.30 Å, of which ten are < 2.10 Å. The contacts H(262)...H(81), 1.94 and H(281)...H(272), 2.02 Å, are common to both forms; in form *F* these are also short: H(72)...H(151), 1.99, H(122)...H(192), 2.00 and H(261)...H(222), 2.01 Å. With the FF parameters used here, form *S* has a slightly higher nonbonded energy than *F*, ~ 1.65 kJ mol⁻¹.

The most interesting results from the calculations are the angle-bend and torsion energies. Table 6 shows that the *S* form has a considerably higher torsion energy than *F*, ~ 20.4 kJ mol⁻¹. The largest contributions arise from strong 1,2-diaxial repulsions about the C-C bonds 17-18 and 20-21. The corresponding energy, 22.03 kJ mol⁻¹, is about 37% of the total torsion strain energy. There are similar interactions, but less severe about the bonds 14-15 and 15-16. In comparison, the largest torsion energy about a C-C bond in form *F* comes from the 16-17 bond, ~ 6.4 kJ mol⁻¹ ($\sim 16\%$). A larger fraction of the strain in the *D/E* end of this form goes into distortions of valency angles. The

* Superscripts refer to the symmetry code given in the legend of Fig. 3.

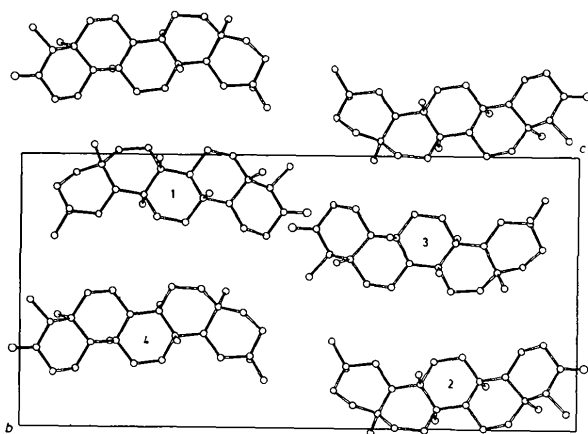


Fig. 3. Packing of the molecules along *a* and rotated 5° about *c*. Numbering of molecules corresponds to the following symmetry code: (1) *x, y, z*; (2) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (3) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (4) $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

C—C—C angles 15–16–17, 116.8, 13–18–19, 116.6, 13–18–17, 117.0 and 18–19–20, 120.1°, are significantly increased over the parent 'strain-free' values; and the three C—C—H angles at C(18) are contracted correspondingly, range 101.8–104.2°. Excluding 17–18–19 at 112.1°, the valency angles at C(18) and the very large angle 18–19–20 represent together a strain energy of 18.66 kJ mol⁻¹, which is 25% of the total angle-bend energy. This total is ~17.4 kJ mol⁻¹ less in form *S*, where each of the angles 9–8–14, 14–15–16 and 15–16–17 contributes to the strain by about the same amount, 2.3–2.5 kJ mol⁻¹.

The total strain energies of *S* and *F* differ by only ~3.85 kJ mol⁻¹, with *F* lower than *S*. This is the same order as found previously for structure (VI), but there with a larger difference, ~7.75 kJ mol⁻¹. We are led to the conclusion that the *S* and *F* forms of the friedelane system are very similar in energy, but with *F* slightly more favoured than *S*. The conformational preference of a given derivative must be sensitive both to changes in substitution and in the crystalline environment.

The calculations show that Dreiding models are insufficient for evaluating such complicated conformational problems. In particular, these rigid models do not represent 1,2-diaxial repulsions properly. On the other hand, they seem to exaggerate the strain associated with distortions of valency angles.

Concluding remarks

X-ray studies of 14 derivatives of friedelane or closely related triterpenes have shown that both forms *S* and *F* occur in the crystalline state. In some instances the preference for a particular form can be rationalized, but other observations are more puzzling. Friedelan-3β-ol (*Ib*) for instance, is *S*, while a derivative of the α-epimer (*Ic*) appears to be *F*. Campanulin (VI) which is *F* in the crystal can be synthesized from friedelin *via* (*Ib*) (Torii, Tachibana, Yamada, Tsuyuki & Takahashi, 1975); (VIII) (*S*) can be synthesized from (VI) (*F*) *via* alnus-5-en-3β-ol (Tori *et al.*, 1983). The reactions do not involve rings *D* and *E*.

Friedelin has the *S* form in the crystal. FF calculations for the isolated molecule predicted *F* lower in energy than *S* by 3.85 kJ mol⁻¹. This is the same order as found for (VI), but the energy difference in friedelin is less by a factor of two. The small magnitude makes a definitive ranking of the two forms difficult, but rather emphasizes their similarity in energy and stability. This result is not evident from model building. In the crystalline state the preference for any one of the two forms is determined also by the intermolecular forces (crystal packing); furthermore, a change in substitution could easily bring about a change of conformation.

The combined X-ray and FF studies of two triterpenes have demonstrated the ability of FF

methods to calculate the geometry of such complex molecules with an accuracy comparable to that of many structure analyses.

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Crystal Structure of 1-Methyluracil from Neutron Diffraction at 15, 60 and 123 K

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Abstract

The crystal structure of 1-methylpyrimidine-2,4-dione (1-methyluracil, $C_5H_6N_2O_2$) has been determined at 15, 60 and 123 K from neutron diffraction data. Molecules lie in the eightfold special positions (symmetry m) of space group $Ibam$, with $a = 13.213$ (2), $b = 13.172$ (2), $c = 6.163$ (1) Å at 15 K. Full-matrix least-squares refinements based on 807 (15 K), 805 (60 K) and 815 (123 K) reflections with $\sin\theta/\lambda < 0.69$ Å⁻¹ converged with $R(F^2) = 0.023$, 0.024 and 0.024 respectively. Bond lengths and angles have e.s.d.'s less than 0.002 Å and 0.2°. Detailed analysis of the anisotropic thermal parameters gives estimates of the zero-point internal vibrations for all nuclei and also for molecular rigid-body thermal vibrations at 15, 60 and 123 K. With thermal-vibration corrections there is good agreement in bond lengths and angles at the three temperatures.

Introduction

The crystal structure of 1-methyluracil (Fig. 1) was determined by Green, Mathews & Rich (1962) from X-ray diffraction data, presumably at room temperature. Neither the details of the analysis, nor the atomic parameters have been published. This is an important crystal structure because it contains the uracil moiety in an environment with similarities to that of uracil in ribonucleic acids. It was chosen for a study aimed at providing highly accurate molecular dimensions because the structure is simple and good quality crystals are easily grown. The structure has been determined from neutron diffraction data collected at

15, 60 and 123 K. The purpose in obtaining the structure at a sequence of low temperatures was to aid our efforts in understanding the thermal vibrations in the crystal and the effects which they have on the apparent molecular dimensions.

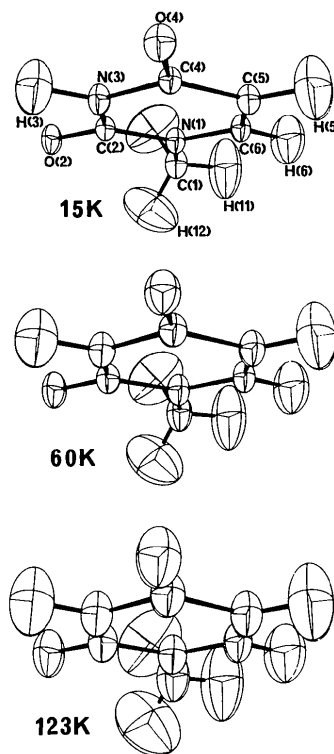


Fig. 1. Atomic labeling and thermal ellipsoids for 1-methyluracil shown at 95% probability level (Johnson, 1976).