Crystal Structure Analysis and Strain-energy Minimization Calculations on a Sterically Crowded Molecule: 1,8-Dimethylnaphthalene

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The crystal structure of 1,8-dimethylnaphthalene has been solved by a reciprocal space-search method. Least-squares refinement of 914 independent *X*-ray reflections measured on a diffractometer leads to *R* 0·080. The molecular distortions caused by steric interaction of the methyl groups have been analysed by means of strain-energy minimization calculations, which show that the repulsive energy between the methyl groups is reduced mainly by bond-angle distortion at the junction between the methyl groups and the naphthalene nucleus. Crystals are monoclinic, space group $P2_1/c$, $Z = 4$, $a = 9{\cdot}835(3)$, $b = 7{\cdot}012(3)$, $c = 16{\cdot}115(5)$ Å, $\beta = 124{\cdot}35(3)°$.

In recent years the techniques of calculating the minimum conformational potential energy of molecules have been further extended. For example, there is a strain-energy minimization procedure[1] which enables all the independent molecular co-ordinates to be varied simultaneously. This technique has been successfully applied to conformational problems in both organic[1] and inorganic[2] chemistry. However, the choice of suitable potential functions and the generality of this technique still poses some problems.

The present combined *X*-ray and conformational study of 1,8-dimethylnaphthalene provides another opportunity to test potential functions and the minimization procedure, since molecular models and the related structure of 3-bromo-1,8-dimethylnaphthalene,[3] suggest that there is appreciable steric interaction between the methyl substituents.

EXPERIMENTAL

We collected two sets of *X*-ray intensity data. The first was obtained from a rather small crystal and proved adequate for solving the structure, but on refinement we found that these data did not define the structure with sufficient precision to warrant a meaningful comparison with the results from the strain-energy minimization procedure. We therefore collected a second data set of better quality from a somewhat larger crystal in the manner described here.

Slow evaporation of a solution of 1,8-dimethylnaphthalene in acetone yielded transparent off-white single crystals. Preliminary space-group data were obtained from precession photographs. A least-squares fit of θ, $-\theta$ values measured for several reflections using Mo-K_α radiation gave the cell dimensions.

Crystal Data.—$C_{12}H_{12}$, $M = 156{\cdot}1$. Monoclinic, $a = 9{\cdot}835(3)$, $b = 7{\cdot}012(3)$, $c = 16{\cdot}115(5)$ Å, $\beta = 124{\cdot}35(3)°$, $U = 917{\cdot}53$ Å^3, $Z = 4$, $D_c = 1{\cdot}13$ g cm^{-3}. Space group $P2_1/c$ from systematic absences: $h0l$, $l = 2n$; $0k0$, $k = 2n$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; $\mu(\text{Mo-}K_\alpha) = 0{\cdot}69$ cm^{-1}.

A suitable crystal of dimensions *ca.* $0{\cdot}7 \times 0{\cdot}35 \times 0{\cdot}2$ mm was selected and mounted with gum arabic inside a Lindemann glass capillary. It was aligned along 001 on a three-circle Nonius automatic diffractometer and the intensities of 914 independent reflections significantly above background with $\theta < 25°$ were measured using θ—2θ scans with zirconium-filtered Mo-K_α radiation. Backgrounds were measured for half the scan time at each end of the scans. A control reflection was monitored regularly and its intensity was found to decrease during data collection. This effect was compensated for during refinement by the method of Ibers.[4] Intensities were corrected for Lorentz and polarization effects but not for absorption. The standard deviation, $\sigma(I)$, of an intensity I was estimated from the expression: $\sigma(I) = [\text{total counts} + \text{total background counts} + (0{\cdot}35 \times \text{net counts})^2]^{\frac{1}{2}}$. The standard deviation, $\sigma(F)$, of a structure amplitude F was then taken to be $\sigma(F^2)/(2F)$, and the weights for the least-squares refinements were taken to be $1/\sigma^2(F)$.

Solution and Refinement of The Crystal Structure.—The crystal structure was determined from the initial poor-quality data set by means of Fourier transform fitting procedures.[5,6] The three-dimensional rotation function[5] produced a clear indication of the orientation of the molecule. Tollin's *Q*-function[6] for the *c* glide plane also unambiguously located the distance of the molecule from the *c* glide, thus fixing the atomic *y* co-ordinates, but in the *Q*-function for the 2_1 axis it proved difficult to decide between two possible positions, (x, z) and $(x, \frac{1}{4} + z)$. Possibly this was due to the preponderance of $h0l$ data (30%) in the initial data set. Consideration of the packing schemes of the two models did not give a clear indication which would be the correct choice.

The correct location of the molecule with respect to the 2_1 axis was determined by refining one of the two possible structures by least-squares and then examining *R* as a function of *l*. For this trial structure, refinement terminated with a rather poor overall agreement index, *R* 36·3%. The agreement for the reflections with $l = 2n$ was better (*R* 27·6%), but that for the reflections with $l = 2n + 1$ extremely poor (*R* 50·4%). Clearly this was the incorrect structure.

The alternative structure was then refined. Convergence was achieved at *R* 21·6% with isotropic temperature parameters; refinement with anisotropic thermal parameters reduced *R* to 12·2%. A difference electron-density synthesis at this stage showed the presence of all hydrogen atoms, and inclusion of these in the model, with subsequent refinement of the carbon parameters, resulted in *R* 10·1%.

Distances and angles were next examined and it was clear from the discrepancies between chemically equivalent bond distances that the quality of our intensity data was insufficient to warrant a comparison of the observed structure with the strain energy minimization results. We therefore also collected a second set of intensity data, as described, in order to obtain more accurate structure parameters.

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[1] R. H. Boyd, *J. Chem. Phys.*, 1968, **49**, 2574.

[2] D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and M. R. Snow, *J. Amer. Chem. Soc.*, 1970, **92**, 3617.

[3] M. B. Jameson and B. R. Penfold, *J. Chem. Soc.*, 1965, 525.

[4] J. A. Ibers, *Acta Cryst.*, 1969, **B25**, 1667.

[5] P. Tollin and W. Cochran, *Acta Cryst.*, 1964, **17**, 1322.

[6] P. Tollin, *Acta Cryst.*, 1966, **21**, 613.

TABLE 1

Final least-squares fractional co-ordinates and thermal parameters *

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0·24739(7)	−0·06341(9)	0·45864(4)	0·01552(11)	0·03055(31)	0·00637(4)	−0·00389(11)	0·00463(6)	−0·00066(7)
C(2)	0·16643(9)	0·05446(13)	0·48398(6)	0·01965(14)	0·04233(37)	0·00903(6)	−0·00349(16)	0·00710(8)	−0·00233(11)
C(3)	0·09157(10)	0·22297(14)	0·43341(8)	0·01914(14)	0·04529(39)	0·01103(7)	−0·00124(17)	0·00749(9)	−0·00611(13)
C(4)	0·09898(8)	0·27707(13)	0·35591(7)	0·01716(13)	0·03078(35)	0·01041(7)	0·00139(14)	0·00309(8)	−0·00136(11)
C(5)	0·18941(10)	0·22369(15)	0·24424(6)	0·02079(15)	0·04074(39)	0·00696(5)	−0·00469(16)	0·00223(7)	0·00405(10)
C(6)	0·26862(12)	0·11779(18)	0·21487(6)	0·02876(19)	0·06086(46)	0·00704(6)	−0·00890(23)	0·00728(9)	0·00133(13)
C(7)	0·34392(10)	−0·05278(15)	0·26392(6)	0·02387(16)	0·05121(41)	0·00743(5)	−0·00317(17)	0·00722(8)	−0·00215(11)
C(8)	0·34105(7)	−0·12031(10)	0·34236(5)	0·01597(11)	0·03244(33)	0·00682(4)	−0·00426(13)	0·00441(6)	−0·00248(8)
C(9)	0·25927(6)	−0·01136(8)	0·37672(4)	0·01349(10)	0·02367(29)	0·00528(3)	−0·00160(10)	0·00343(5)	−0·00015(7)
C(10)	0·18400(7)	0·16429(9)	0·32623(4)	0·01507(11)	0·02843(31)	0·00671(4)	−0·00289(12)	0·00326(6)	−0·00027(8)
C(11)	0·31972(14)	−0·24257(15)	0·52095(8)	0·03258(22)	0·03782(39)	0·00904(6)	−0·00324(19)	0·00840(9)	0·00409(11)
C(12)	0·42645(14)	−0·30965(13)	0·38641(11)	0·02988(20)	0·02924(34)	0·01509(10)	0·00496(17)	0·01270(13)	0·00484(12)
				B/Å^2					
H(2)	0·151(1)	0·018(2)	0·535(1)	12·5(4)					
H(3)	0·033(1)	0·306(2)	0·454(1)	13·6(4)					
H(4)	0·058(1)	0·392(2)	0·322(1)	11·0(4)					
H(5)	0·134(1)	0·345(2)	0·221(1)	11·1(4)					
H(6)	0·264(2)	0·160(2)	0·161(1)	13·3(4)					
H(7)	0·407(1)	−0·130(2)	0·242(1)	13·2(4)					
H(11A)	0·446(2)	−0·264(2)	0·545(1)	13·5(4)					
H(11B)	0·274(2)	−0·366(2)	0·480(1)	12·6(4)					
H(11C)	0·301(2)	−0·243(2)	0·566(1)	13·5(5)					
H(12A)	0·524(2)	−0·297(2)	0·458(1)	13·3(5)					
H(12B)	0·347(2)	−0·410(2)	0·386(1)	12·9(4)					
H(12C)	0·448(2)	−0·349(2)	0·344(1)	13·5(5)					

* The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2\,hk\beta_{12} + 2\,hl\beta_{13} + 2\,kl\beta_{23})]$.

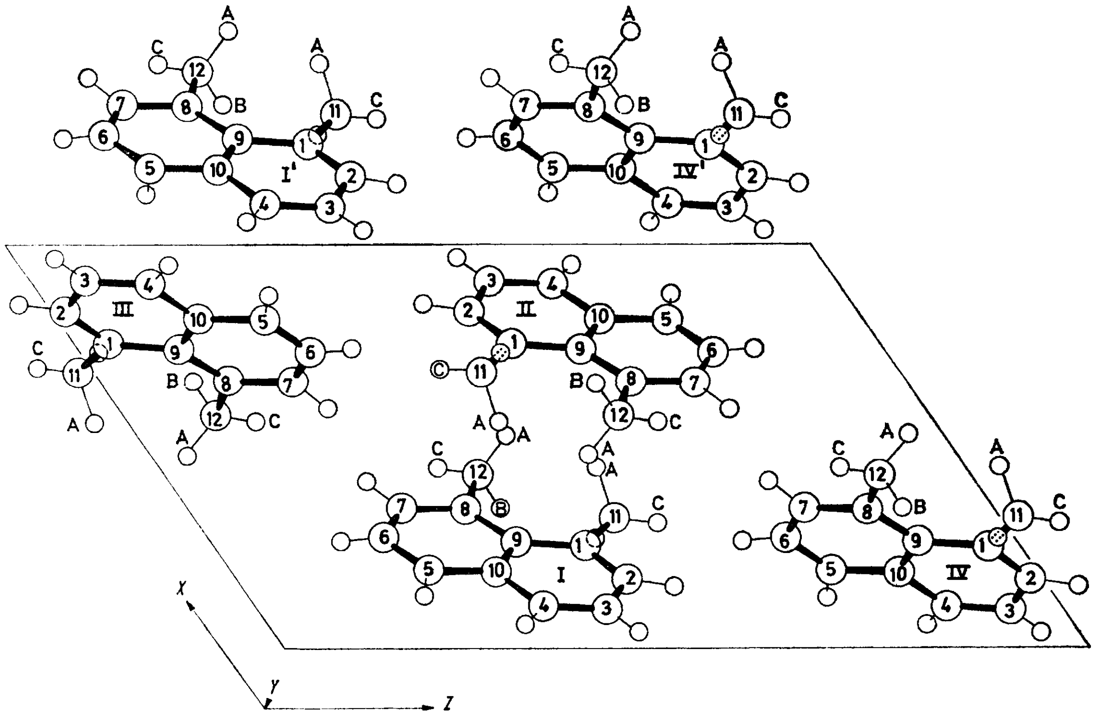


FIGURE 1 Projection of the structure viewed down the b axis. Molecule I is at x, y, z, I′ at $1 + x, y, z$, II at $1 - x, 1 - y, 1 - z$, III at $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$, IV at $x, \frac{1}{2} - y, \frac{1}{2} + z$, and IV′ at $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$

Anisotropic refinement of the carbon parameters with the new data set resulted in R 11·7%. Subsequent examination of a difference electron-density map showed that the peaks due to the hydrogen atoms were in the same positions as before. The hydrogen atoms were then included and refined with isotropic temperature factors. The final conventional and weighted R factors based on F were 8·0 and 7·2% respectively. The agreement between bond lengths and angles for chemically equivalent atoms was good and we concluded that these parameters were suitable for comparison with the theoretical model.

Final atomic parameters are listed in Table 1. Final values of F_o and F_c are listed in Supplementary Publication No. SUP 20825 (3 pp.).* Scattering factors for carbon and hydrogen were taken from ref. 7.

Strain-energy Minimization Calculation.—Strain-energy minimization techniques have been applied to the 1,8-dimethylnaphthalene molecule in an attempt to account for the distorted molecular geometry found by *X*-ray analysis. The method of calculation has been described in detail previously.[1] In summary, the total molecular strain energy, *U*, is assumed to be represented by a five-term summation:

$$U = \sum_{\mathrm{ij}} U(r_{\mathrm{ij}})_{\mathrm{nb}} + \sum_{\mathrm{ij}} U(r_{\mathrm{ij}})_{\mathrm{b}} + \sum_{\mathrm{ijk}} U(\phi_{\mathrm{ijk}}) + \sum_{\mathrm{ijkl}} U(\phi_{\mathrm{ijkl}}) + \sum_{\mathrm{ijkm}} U(\delta_{\mathrm{ijkm}})$$

The first term $U(r_{ij})_{nb}$ describes intramolecular non-bonded interactions and is usually a function of the type:[6]

$$U(r_{\mathrm{ij}})_{\mathrm{nb}} = a_{\mathrm{ij}} \exp\,(-b_{\mathrm{ij}}r_{\mathrm{ij}}) - c_{\mathrm{ij}}/r_{\mathrm{ij}}^{6}$$

where a_{ij}, b_{ij}, and c_{ij} are constant terms for a particular type of intramolecular interaction. $U(r_{ij})_b$ and $U(\theta_{ijk})$, account for bond stretching and bond angle distortions, respectively. Both terms are approximated by the quadratic form:

$$U(P) = \tfrac{1}{2}Q(PO - P)^2$$

where *PO* is the strain-free value of the bond length or angle concerned, and *Q* the appropriate force constant. $U(\phi_{jikl})$, accounts for the restriction to rotation about C=C double bonds. We used a two-fold potential function of the form:

$$U(\phi_{\mathrm{ijkl}}) = \tfrac{1}{2}V_{\mathrm{ijkl}}\,[1 - \cos\,(2\phi_{\mathrm{ijkl}})]$$

where V_{ijkl} is the height of the potential barrier to rotation of atom i with respect to atom l about the bond jk.

The last term, $U(\delta_{ijkm})$, accounts for the energy of deformation of a bond to a substituent atom, m, from the plane of an aromatic ring to which the atoms i, j, and k belong, and has the form:

$$U(\delta_{\mathrm{ijkm}}) = \tfrac{1}{2}K_{\mathrm{ijkm}}\delta^{2}_{\mathrm{ijkm}}$$

where K_{ijkm} is the deformation constant.

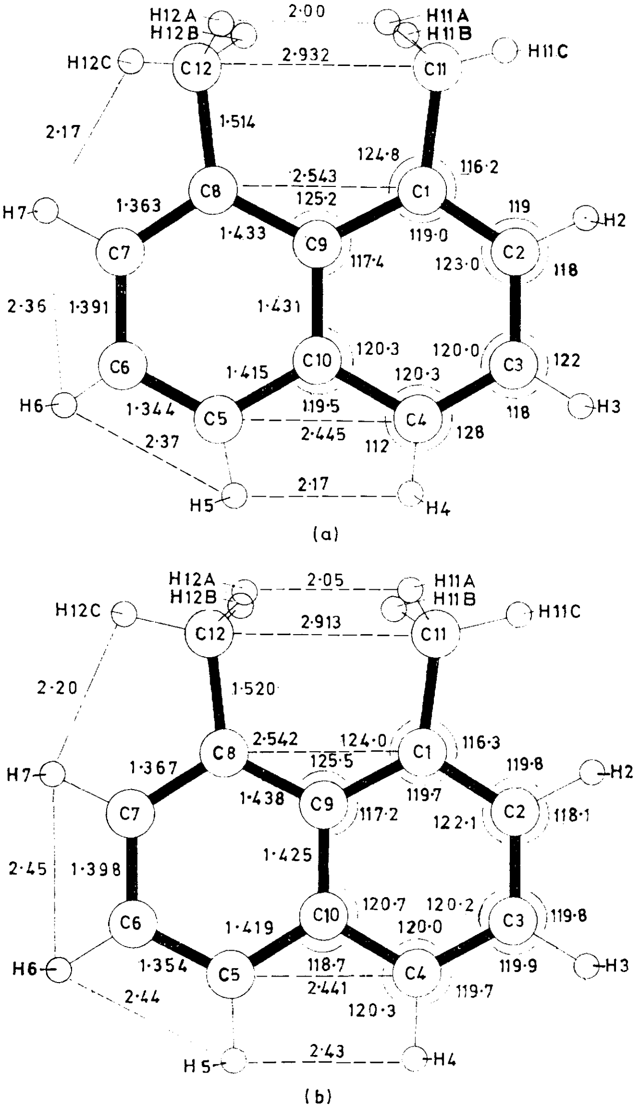
The parameters employed (Table 5) are similar to those used for strain-energy calculations on cyclophanes.[4] Minimization of the total strain-energy was achieved by means of a modified Newton–Raphson method of optimization.[4]

Initial co-ordinates for the minimization procedure were based on the parameters reported for unsubstituted naphthalene. A Cartesian molecular co-ordinate system was chosen with the origin in the centre of the C(9)–C(10) bond, and the *X* and *Y* axes parallel with the directions C(9)–C(2) and C(10)–C(9), respectively. For each cycle of refinement approximately 100 interactions were included for the optimization of 66 independent parameters. During the early stages of refinement it was found necessary to introduce damping factors to maintain convergence towards a minimum energy molecular geometry.

Final minimized co-ordinates for the molecule are given in Table 6. A comparison of mean bond lengths and angles (assuming molecular symmmetry *mm*2) for the observed and calculated molecular geometries is given in Figure 2.

DISCUSSION

Description of The Crystal Structure.—The crystal structure is built up of well-separated molecules. The shortest intermolecular C · · · C contact distance (3·68 Å) is between C(2) and C(2′) across a centre of symmetry. A projection of the structure on (010) is shown in Figure 1. Interatomic distances and angles are listed together with their standard deviations in Tables 2 and 3, respectively.



(a)

(b)

FIGURE 2 Perspective views of the molecule showing averaged bond lengths and angles from (a) *X*-ray structure analysis and (b) strain-energy minimization calculation

As expected, the strong non-bonded interaction between the methyl substituents [C(11) · · · C(12) 2·93 Å] results in considerable distortions of the molecular geometry. The most marked distortions occur at the junctions of the methyl groups with the naphthalene

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[7] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1969.

nucleus. The inner angles [C(9)–C(1)–C(11) and C(9)–C(8)–C(12)] are increased from the ideal 120° to almost 125° while the outer angles [C(2)–C(1)–C(11) and C(7)–C(8)–C(12)] are decreased to 116°.

TABLE 2

Observed interatomic distances (Å)

(*a*) C–C Bonding distances

C(1)–C(2)	1·360(1)	C(7)–C(8)	1·365(1)
C(1)–C(9)	1·437(1)	C(8)–C(9)	1·428(1)
C(1)–C(11)	1·512(1)	C(8)–C(12)	1·516(1)
C(2)–C(3)	1·388(2)	C(6)–C(7)	1·394(2)
C(3)–C(4)	1·346(1)	C(5)–C(6)	1·341(2)
C(4)–C(10)	1·416(1)	C(5)–C(10)	1·415(1)
C(9)–C(10)	1·431(1)		

(*b*) C–H Bonding distances

C(2)–H(2)	0·95(2)	C(7)–H(7)	1·02(2)
C(3)–H(3)	1·00(2)	C(6)–H(6)	0·90(2)
C(4)–H(4)	0·93(2)	C(5)–H(5)	0·96(2)
C(11)–H(11A)	1·08(2)	C(12)–H(12A)	1·01(2)
C(11)–H(11B)	1·02(2)	C(12)–H(12B)	1·05(2)
C(11)–H(11C)	0·84(2)	C(12)–H(12C)	0·87(2)

(*c*) Important non-bonding distances

C(11) · · · C(12)	2·932(2)	H(4) · · · H(5)	2·17(2)
C(1) · · · C(8)	2·543(1)	C(4) · · · C(5)	2·445(2)
H(11A) · · · H(12A)	1·96(2)	H(11B) · · · H(12B)	2·03(2)
H(2) · · · H(11C)	2·22(2)	H(7) · · · H(12C)	2·12(2)
H(2) · · · H(3)	2·33(2)	H(7) · · · H(6)	2·40(2)
H(3) · · · H(4)	2·35(2)	H(6) · · · H(5)	2·38(2)
C(1) · · · C(12)	3·123(2)	C(8) · · · C(11)	3·121(2)

TABLE 3

Observed interatomic angles (°)

C(2)–C(1)–C(9)	119·1(1)	C(9)–C(8)–C(7)	118·9(1)
C(2)–C(1)–C(11)	116·2(1)	C(7)–C(8)–C(12)	116·2(1)
C(9)–C(1)–C(11)	124·7(1)	C(9)–C(8)–C(12)	124·8(1)
C(1)–C(2)–C(3)	123·2(1)	C(6)–C(7)–C(8)	122·7(1)
C(2)–C(3)–C(4)	119·8(1)	C(5)–C(6)–C(7)	120·2(1)
C(3)–C(4)–C(10)	120·5(1)	C(10)–C(5)–C(6)	120·1(1)
C(1)–C(9)–C(8)	125·2(1)	C(4)–C(10)–C(5)	119·5(1)
C(1)–C(9)–C(10)	117·2(1)	C(8)–C(9)–C(10)	117·6(1)
C(4)–C(10)–C(9)	120·2(1)	C(5)–C(10)–C(9)	120·3(1)
C(1)–C(11)–H(11A)	111·5(8)	C(8)–C(12)–H(12A)	112·1(9)
C(1)–C(11)–H(11B)	113·8(8)	C(8)–C(12)–H(12B)	111·9(8)
C(1)–C(11)–H(11C)	109·2(12)	C(8)–C(12)–H(12C)	102·9(11)
C(1)–C(2)–H(2)	120·0(9)	C(8)–C(7)–H(7)	117·7(8)
C(3)–C(2)–H(2)	116·6(9)	C(6)–C(7)–H(7)	119·6(8)
C(2)–C(3)–H(3)	120·8(9)	C(7)–C(6)–H(6)	123·4(10)
C(4)–C(3)–H(3)	119·4(9)	C(5)–C(6)–H(6)	116·2(10)
C(3)–C(4)–H(4)	123·8(9)	C(6)–C(5)–H(5)	131·8(8)
C(10)–C(4)–H(4)	115·6(9)	C(10)–C(5)–H(5)	108·0(9)

TABLE 4

Best least-squares plane through carbon atoms, C(1)—(12).

Equation: $5{\cdot}857x + 3{\cdot}434y + 3{\cdot}057z - 2{\cdot}631 = 0$

Root-mean square deviation: 0·008 Å

Deviations from the plane (Å):

C(1) 0·002, C(2) 0·010, C(3) −0·004, C(4) −0·012, C(5) −0·007, C(6) 0·004, C(7) 0·010, C(8) 0·001, C(9) 0·001, C(10) 0·008, C(11) 0·001, C(12) −0·015, H(2) −0·049, H(3) 0·002, H(4) 0·037, H(5) 0·016, H(6) −0·040, H(7) 0·047, H(11A) 0·741, H(11B) −0·817, H(11C) 0·029, H(12A) 0·821, H(12B) −0·823, H(12C) −0·155

Surprisingly, the carbon skeleton is planar. No carbon atom deviates from the best least-squares plane through the carbon atoms by >0·02 Å (Table 4). One might expect that substituent interaction could be reduced by bending one methyl group above and one below the naphthalene plane, but this does not occur. This contrasts with the situation in 1,4,5,8-tetrachloronaphthalene,[8] where the chlorine atoms were found to be 0·2 Å out of the molecular plane and, in addition, a significant buckling of the naphthalene nucleus was

TABLE 5

Parameters used in strain-energy minimization calculations

(*a*) $U(r_{ij})_{nb}$ (Non-bonded repulsion) [a]

i	j	a_{ij}	b_{ij}	c_{ij}
H	H	45·8	4·08	0·341
C	H	218·0	4·20	0·840
C	C	1640·0	4·32	2·070

(*b*) $U(r_{ij})_b$ (Bond stretching) [b]

i	j	Q_{ij}	PO_{ij} (Å)
C	H	5·05	1·09
C(A)[c]	C(A)	7·65	1·40
C(A)	C(B)	7·65	1·36
C(B)	C(B)	7·65	1·42
C(B)	C(ME)	4·60	1·51

(*c*) $U(\theta_{ijk})$ (Bond-angle deformation) [b]

i	j	k	Q_{ijk}	PO_{ijk} (radians)
C	C	H	0·75	2·094
C	C	C	1·00	2·094
H	C	H	0·55	1·910
C	C	H	0·65	1·910

(*d*) $U(\phi_{ijkl})$ (C=C bond torsion) [d]

i	j	k	l	V_{ijkl}
C	C	C	C	0·208

(*e*) $U(\delta_{ijkm})$ (Out-of-plane bending) [d]

i	j	k	m	K_{ijkm}
C	C	C	H	0·29
C	C	C	C	0·80

[a] Units for parameters a_{ij}, b_{ij}, and c_{ij}: 10^{-11} erg mol^{-1}, Å^{-1}, and 10^{-11} erg Å^6 mol^{-1}. [b] Force constants are given in units of 10^5 dyne cm^{-1}. [c] To simplify the computer specification of the problem for the bonding distances whilst maintaining reasonable correspondence with the strain-free values in the naphthalene nucleus, the atoms were divided into classes as follows: C(2), C(3), C(6), C(7) = C(A); C(11), C(12) = C(ME); the remaining C atoms were designated C(B). [d] Energy barriers are given in 10^{-11} erg.

TABLE 6

Final atomic co-ordinates (Å) from strain-energy minimization calculation

Atom	*X*	*Y*	*Z*
C(1)	1·194	1·390	0·000
C(2)	2·371	0·695	0·000
C(3)	2·408	−0·702	0·000
C(4)	1·257	−1·417	0·001
C(5)	−1·182	−1·522	0·005
C(6)	−2·390	−0·909	0·007
C(7)	−2·473	0·486	0·007
C(8)	−1·360	1·280	0·004
C(9)	−0·055	0·677	0·001
C(10)	0·006	−0·746	0·002
C(11)	1·307	2·906	−0·003
C(12)	−1·603	2·781	0·003
H(2)	3·319	1·234	0·000
H(3)	3·369	−1·220	−0·001
H(4)	1·297	−2·507	0·000
H(5)	−1·129	−2·612	0·005
H(6)	−3·303	−1·507	0·010
H(7)	−3·464	0·942	0·009
H(11A)	0·858	3·321	0·896
H(11B)	0·855	3·318	−0·902
H(11C)	2·354	3·208	−0·005
H(12A)	−1·189	3·232	0·901
H(12B)	−1·191	3·231	−0·897
H(12C)	−2·673	2·992	0·004

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[8] G. Gafner and F. H. Herbstein, *Acta Cryst.*, 1962, **15**, 1081.

observed. In 1,8-diphenylnaphthalene[9] the nucleus is planar, but the phenyl carbons attached to the nucleus are bent 0·06 Å above and below this plane. A buckling of the naphthalene nucleus was also reported for 3-bromo-1,8-dimethylnaphthalene.[3] The reasons for these differences are discussed later.

The configuration of the methyl hydrogen atoms is also unexpected. Instead of being enmeshed in a cogwheel-like system to minimize H · · · H interactions, the two hydrogens on the outside of the C · · · C interaction lie almost in the molecular plane while the remaining hydrogens face each other in pairs such that the H · · · H distances are *ca.* 2·0 Å (see Figure 1).

Comparison of Observed and Calculated Molecular Geometries.—As expected, the strain-energy minimization calculations clearly indicate that there is considerable steric repulsion between the methyl substituents. For the initial geometry, with strain-free bond lengths and angles, calculated non-bonded interactions (distance Å, energy kcal mol^{-1} in parentheses) were: H(11A) · · · H(12A) 1·36 (17·8) H(11B) · · · H(12B), 1·36 (17·8) C(11) · · · C(12), 2·39 (6·2).

This initial repulsive energy between the methyl groups (total 41·8 kcal mol^{-1}) is reduced to a mere 2·1 kcal mol^{-1}, mainly by bond-angle distortion at C(1), C(8), and C(9). This distortion of the bond angles introduces only 6·3 kcal mol^{-1} extra strain energy into the molecule. Thus, overall, the total molecular strain energy is reduced from 41·8 to 8·4 kcal mol^{-1} (Table 7).

TABLE 7

Major terms (>0·3 kcal mol^{-1}) in final minimum energy summation

Non-bonded interactions	Before minimization	After minimization
C(11) · · · C(12)	6·2	0·32
H(11A) · · · H(12A)	17·8	0·88
H(11B) · · · H(12B)	17·8	0·88
H(2) · · · H(11C)	0	0·41
H(7) · · · H(12C)	0	0·41
C(2) · · · H(11C)	0	0·34
C(7) · · · H(12C)	0	0·34
Bond-angle bending		
C(1)–C(9)–C(8)	0	0·66
C(2)–C(1)–C(11)	0	0·30
C(7)–C(8)–C(12)	0	0·30
C(9)–C(1)–C(11)	0	0·35
C(9)–C(8)–C(12)	0	0·35
Total	41·8	5·54

Total minimized strain-energy including all interactions: is 8·43 kcal mol^{-1}.

In general there is good agreement between the observed and calculated molecular geometries. All bond lengths agree within 0·01 Å and all bond angles within 1° with the corresponding crystal structure values.

Further, the calculated molecular co-ordinates correspond with a completely planar molecule as was found by *X*-ray analysis. In particular, there is no tendency for the methyl groups to deviate from the plane of the naphthalene nucleus. In contrast, in 3-bromo-1,8-dimethylnaphthalene[9] and 1,4,5,8-tetrachloronaphthalene[7] the carbon atoms of the naphthalene nucleus are not coplanar. The reason for this difference is not clear but may be associated with halogen substitution at a naphthalene nucleus.[9]

A more recent *X*-ray analysis of a more closely related overcrowded molecule, 1,8-diphenylnaphthalene,[9] agrees with our results insofar as the naphthalene nucleus is found to be planar, but differs in that the phenyl groups are bent above and below the naphthalene plane. This difference may be due to the fact that a small out-of-plane bending angle, (δ_{ijkm}), of the phenyl group results in a relatively large displacement of the *para*-carbon atoms. Thus the C · · · C inter-phenyl repulsive interaction is reduced at the expense of only a small amount of out-of-plane bending energy, $U(\delta_{ijkm})$. In 1,8-dimethylnaphthalene such a small out-of-plane bending angle of the methyl groups would not significantly reduce the C · · · C or H · · · H non-bonded interactions.

As previously discussed, the methyl groups are found from the crystal structure analysis to be in the fixed orientation shown in Figure 1. This orientation is such that the C(11)–H(11C) and C(12)–H(12C) bonds lie practically in the plane of the aromatic rings. The minimization calculations show that this is indeed the most stable configuration for the methyl groups. This was demonstrated by carrying out minimization calculations with different starting orientations of the methyl groups. The resulting minimized geometries all had the same orientation of the methyl groups as found in the crystal structure. This conformation minimizes the H · · · H interactions. Thus the calculations indicate that the fixed orientation of the methyl groups in the crystal structure results from intra-, rather than intermolecular forces.

One feature observed in the crystal structure which was not reproduced in the calculated model was the transmission of the strain between the methyl hydrogens, H(11C), H(12C) and their nearest aromatic neighbouring hydrogens, H(2) and H(7), respectively, around the aromatic nucleus so as to cause a strong interaction between the *peri*-hydrogens H(4) and H(5). In the crystal structure these hydrogens were found to be bent towards one another such that the distance H(4) · · · H(5) [2·17(2) Å] is similar to that of the aromatic–methyl hydrogen interactions [mean of H(11C) · · · H(2) and H(12C) · · · H(7) 2·17(2) Å]. The remaining nearest neighbour H · · · H interactions are all >2·32 Å. In the calculated model only the methyl–aromatic H · · · H interactions show signs of strain (H · · · H 2·20 Å). The aromatic–aromatic H · · · H distances are all close to the strain-free values at about 2·45 Å. Clearly our assumptions concerning the H · · · H interactions are inadequate.

Nevertheless, this study has indicated that the strain parameters developed for cyclophanes[1] are indeed applicable to other systems, at least to provide an understanding of the gross effects in overcrowded molecules.

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[9] R. Ogilvie and A. Parkes, personal communication.