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STRAIN IN TERTIARY BUTYL DERIVATIVES

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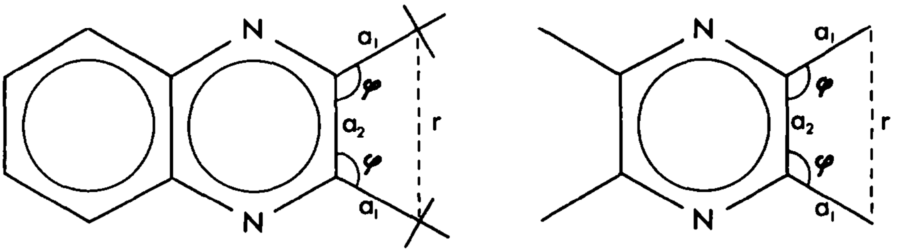
Abstract—Starting from the geometry of the 2,3-di-t-butylquinoxaline molecule repulsion energy curves were obtained for the interaction between two t-Bu groups and between two Me groups. From these curves the geometry and the strain energy have been predicted for a number of t-butyl compounds.

RECENTLY the geometry of *o*-di-t-butyl compounds has been accurately determined by X-ray diffraction.[1,2] This offers the possibility to find the repulsion energy of two t-Bu groups as a function of their distance (Section A) and to predict from this relationship the geometry and strain energy of other *o*-di-t-butyl derivatives (Section B). Similar calculations for tetra-t-butylmethane and related compounds require a more detailed description of the interaction of t-Bu groups in terms of $CH_3 \ldots CH_3$ repulsions. The $CH_3 \ldots CH_3$ repulsion energy curve has been derived from the overall repulsion of the t-Bu groups in 2,3-di-t-butylquinoxaline (Section C).

A qualitative discussion of the bond lengths and angles in 2,3-di-t-butylquinoxaline has been given recently by Visser *et al.*[3]

A. *Repulsion energy of tertiary butyl groups*

In Fig. 1 the geometry of 2,3-di-t-butylquinoxaline (I)[1] is compared with that of 2,3,5,6-tetramethylpyrazine (II).[4] Figures in parentheses denote estimated standard deviations.



I	II
φ = 129·7(0·2)°	φ = 119·8(0·6)°
a_1 = 1·555(0·003) Å	a_1 = 1·505(0·01) Å
a_2 = 1·476(0·003)	a_2 = 1·434(0·01)
r = 3·480(0·003)	r = 3·003(0·01)

FIG. 1 Geometry of 2,3-di-t-butylquinoxaline (I) and 2,3,5,6-tetramethylpyrazine (II).

It is seen that as a result of the repulsion of the t-Bu groups the angle φ is increased by $\delta_1 = 9{\cdot}9\ (0{\cdot}6)^\circ$, the bond lengths a_1 by $\delta_2 = 0{\cdot}050(0{\cdot}01)$ Å and the bond length a_2 by $\delta_3 = 0{\cdot}042\ (0{\cdot}01)$ Å.

If it is assumed that the repulsion energy R of the t-Bu groups is a function only of the distance r between their quaternary C atoms the strain energy of the 2,3-di-t-butylquinoxaline molecule is given by

$$E_s = \sum_i \tfrac{1}{2} k_i \delta_i^2 + R(r) \tag{1}$$

where the quantities k_i are the force constants for bending bond angles and stretching bonds. The summation extends over all relevant angles and bonds, i.e. for 2,3-di-t-butylquinoxaline two angles φ, two bonds a_1 and one bond a_2.

For the molecule in its equilibrium configuration we have the equations

$$\frac{\partial E_s}{\partial \delta_i} = k_i \delta_i + \frac{dR}{dr}\frac{\partial r}{\partial \delta_i} = 0 \tag{2}$$

where the quantities $\partial r/\partial \delta_i$ are known from the geometry of the molecule. Approximate values for the force constants were derived from the literature[5–8] and are listed in Table 1.

TABLE 1. FORCE CONSTANTS USED AND dR/dr VALUES OBTAINED

	k_i^a	dR/dr^b
	16×10^{-12}	$-2{\cdot}35 \times 10^{-4}$
—	3×10^{5}	$-2{\cdot}35 \times 10^{-4}$
=	8×10^{5}	$-3{\cdot}3 \times 10^{-4}$

[a] in dyne.cm.rad.$^{-2}$ for the angles and in dyne.cm^{-1} for the bonds

[b] in dynes

The values for dR/dr following from the three Eqs (2) when the experimental δ_i values are inserted, are given in the last column of Table 1. They agree better than could be expected from the rather large uncertainties in the values of k_i and δ_i. We adopted an average value:

$$dR/dr = -2{\cdot}5 \times 10^{-4} \text{ dynes} = -36 \text{ kcal.mol.}^{-1}\,\text{Å}^{-1} \tag{3}$$

The value of R itself can be estimated from heats of combustion. These data indicate for o-di-t-butylbenzene a total strain energy E_s of about 20 kcal.mol.$^{-1}$ [9,10] We estimated a slightly smaller value, 18 kcal.mol^{-1}, for 2,3-di-t-butylquinoxaline because the steric hindrance of o-t-Bu substituents in a pyrazine ring is expected to be slightly less than in a benzene ring. An indication for this is the fact that in 2,3,5,6-tetramethylpyrazine the distance of o-substituted Me groups (3·003 Å) is somewhat larger than in o-di-methylbenzene (2·91 Å). Substituting in Eq. (1) 18 kcal for E_s and the known values for k_i and δ_i one obtains

$$18 = 7{\cdot}1 + 1{\cdot}1 + 1{\cdot}0 + R(3{\cdot}48)$$

where the figures at the right hand side refer to the bending of φ, the extension of a_1

and the extension of a_2 respectively. From this it follows that

$$R(3{\cdot}48) \approx 9\ \text{kcal} \tag{4}$$

Combining Eqs (3) and (4) we find for $r \approx 3{\cdot}48$ Å

$$R(r) = 9 - 36(r - 3{\cdot}48)\ \text{kcal}$$

or, extrapolating exponentially,

$$R(r) = 9 \exp\left[-4(r - 3{\cdot}48)\right]\ \text{kcal} \tag{5}$$

B. *Calculation of the equilibrium configuration and strain energy of some aromatic* ortho-*di-tertiary butyl derivatives and 1,2-di-tertiary butylethene*

Knowing $R(r)$ from Eq. (5), the equilibrium configuration and strain energy can be predicted for compounds other than 2,3-di-t-butylquinoxaline by applying Eqs (2) and (1). The force constants of Table 1 were used and, for ethene, a bending constant of 8×10^{-12} and double bond stretching constant of 10^6. Examples of the results are given in Table 2. The φ and a values calculated for *o*-di-t-butylbenzene are in agreement with those observed in 1,2,4,5-tetra-t-butylbenzene by Van Bruynsvoort *et al.*[2] which amount to ∠C—C—tb = 130(0·5)°, C—tb = 1·567(0·008) Å and C—C = 1·416(0·008) Å respectively.

TABLE 2. CALCULATED EQUILIBRIUM CONFIGURATIONS AND STRAIN ENERGIES

		∠C—C—tb	C—tb	C—C	R kcal	E_s kcal
2,3-di-t-butyl	δ(°, Å)	10·7	0·053	0·031		
quinoxaline	φ, a(°, Å)	130·5	1·558	1·465		
	$\frac{1}{2}k\delta^2$(kcal)	8·0	1·2	0·6	8·8	18·6
o-di-t-butyl	δ	10·6	0·053	0·031		
benzene	φ, a	130·6	1·573	1·430		
	$\frac{1}{2}k\delta^2$	7·9	1·2	0·6	9·4	19·1
3,4-di-t-butyl	δ	8·3	0·044	0·024		
thiophene	φ, a	131·8	1·564	1·459		
	$\frac{1}{2}k\delta^2$	4·8	0·8	0·3	6·8	12·7
3,4-di-t-butyl	δ	6·8	0·034	0·021		
pyrrole	φ, a	133·3	1·554	1·450		
	$\frac{1}{2}k\delta^2$	3·3	0·3	0·3	6·0	10·1
3,4-di-t-butyl	δ	6·1	0·035	0·019		
furan	φ, a	133·8	1·555	1·459		
	$\frac{1}{2}k\delta^2$	2·6	0·5	0·2	5·4	8·7
1,2-di-t-butyl	δ	11·7	0·037	0·016		
ethene	φ, a	136·1	1·557	1·356		
	$\frac{1}{2}k\delta^2$	4·8	0·6	0·2	5·5	11·1

C. *Configuration and strain energy of, hypothetical, aliphatic tertiary butyl derivatives*

Non bonded methyl–methyl interaction. A straightforward calculation by Eqs (1), (2) and (5) of the strain energy in $C(tb)_4$, $C_2(tb)_6$ and $\cdot C(tb)_3$ leads to the values 308, 450 and 143 kcal.mol^{-1} respectively. It is easily seen, however; that these values are far too high because at a given distance of the quaternary C atoms of two t-Bu groups the average distance of the Me groups increases appreciably when the angle between the bonds with which the t-butyls are attached to the rest of the molecule increases. Now, in the aliphatic compounds considered this angle is about 110–120° whereas in the derivatives considered in Section B it is only 80–90° approximately. Therefore, for the aliphatic compounds, we have calculated the repulsion of the various t-Bu groups in more detail by considering the repulsion of the CH_3 constituents separately.

Interaction of two methyl groups. The overall repulsion of the two t-Bu groups in 2,3-di-t-butylquinoxaline is given by (5). This repulsion consists of three $CH_3 \ldots CH_3$ contacts at a distance of 3·40 Å, two $CH_3 \ldots C$ contacts at 3·45 Å and one $C \ldots C$ contact at 3·50 Å. It was estimated that the three $CH_3 \ldots CH_3$ contacts are responsible for about 90% of the repulsion energy since the other contacts are at larger distances and involve a smaller number of H atoms. With this assumption the repulsion energy of two non bonded methyl groups at a distance r_m is represented by

$$R_m = 1/3 \times 8{\cdot}1 \exp\left[-4(r_m - 3{\cdot}40)\right] = 2{\cdot}7 \exp\left[-4(r_m - 3{\cdot}40)\right] \qquad (6)$$

This relationship is practically identical with that for the repulsion of methane molecules as obtained by Hill[11] from an extrapolation of measurements of the second virial coefficient. The repulsion energies given by Eq. (6) are, however, much higher than the $CH_3 \ldots CH_3$ repulsion energies as estimated by Hill on the basis of an empirical Van der Waals radius of CH_3.

A calculation of equilibrium configuration and strain energy of $C(tb)_4$ and $\cdot C(tb)_3$ along lines similar to those followed in Section B but using Eq. (6) instead of Eq. (5) has led to the results listed in Table 3. Since $C \ldots CH_3$ and $C \ldots C$ interactions were neglected the δ, R and E_s values obtained are probably lower limits of the true values.

TABLE 3. EQUILIBRIUM CONFIGURATION AND STRAIN ENERGY IN $C(tb)_4$ and $.C(tb)_3$

		$\angle$ C—C—CH_3	C—C	R kcal	E_s kcal
$C(tb)_4$	δ(°, Å)	10·0	0·20		
	φ, a(°, Å)	119·6	1·74		
	$\frac{1}{2}k\delta^2$(kcal)	49	35	52	136
$\cdot C(tb)_3$	δ	7·0	0·09		
	φ, a	116·5	1·60		
	$\frac{1}{2}k\delta^2$	19	6	31	56

As expected the strain energies, 136 and 56 kcal respectively, are far smaller than the values, 308 and 143 kcal, obtained from Eq. (5); the reduction factor amounting to 0·44 in the case of $C(tb)_4$ and to 0·39 in the case of $\cdot C(tb)_3$. Assuming for $C_2(tb)_6$, where the detailed calculations would be very complicated, a reduction factor of 0·44 the expected lower limit of the strain energy in this compound would be 0·44 × 450 ≈ 200 kcal. This means that in the hypothetical reaction

$$C_2(tb)_6 \rightarrow 2.C(tb)_3$$

the strain energy would decrease by about 90 kcal.

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