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THE DYNAMIC BEHAVIOUR OF 1,8-DI-t-BUTYLNAPHTHALENE AND ITS GROUP IVA [$(CH_3)_3M$] ANALOGUES: AN EMPIRICAL FORCE FIELD STUDY

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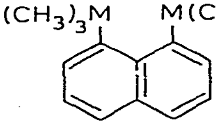
Summary

The results of empirical force field calculations on 1,8-di-t-butylnaphthalene (C_2 ground state symmetry) and its Sn and Si analogues are consistent with experiment in the case of the first two and predict the latter to behave similarly. Torsion of one $(CH_3)_3M$ group does not cause torsion of the other nor enantiomerization. Besides the rate determining energy maximum, each molecule traverses a secondary energy maximum during one automerization cycle, the corresponding secondary minimum energy conformation having C_1 symmetry.

This study was prompted by a report [1] of the dynamic behaviour of II and III, in which a high barrier was inferred for rotation about the Si—naphthalene bonds of II relative to those for the corresponding C—C and C—Sn bonds of I [2] and III [1], respectively. We used the empirical force field (EFF) method in an attempt to delineate the factors specific to Si which were responsible for the anomalous behaviour of II. However, after completion of our own work, we learned that the compound believed to be II is, in fact, the isomer 2-[1-naphthyl]-2,4,4-trimethyl-2,4-disilapentane [3]. Our results therefore afford a first estimate of the barrier to group rotation in II.



(I) M = C
(II) M = Si
(III) M = Sn

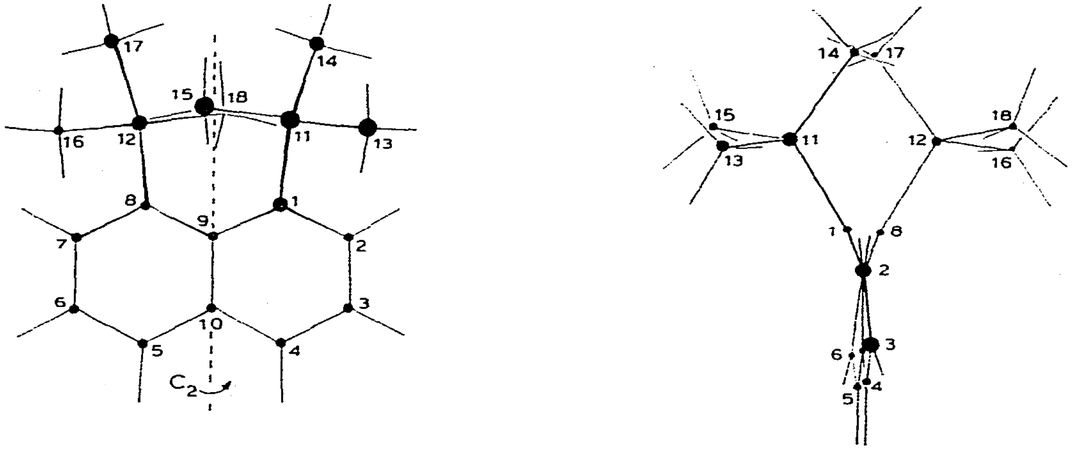


Fig. 1. Ground state of II. (a) viewed perpendicular to the 2, 7, 10 plane; (b) viewed along the 2, 7 line.

The EFF employed has been described previously [4]. Energies were minimized using pattern minimization [5]. Computation used the programme BIGSTRN modified for use on the CDC 7600 at U.M.R.C.C. The naphthalene nucleus was modelled by two condensed benzene rings and the corresponding parameters are those derived specifically for benzenoid hydrocarbons [4] *. Dynamic properties were probed by incremental group driving [4] **. Si and Sn have been modelled by increasing only the relevant preferred bond lengths (r_0) for carbon, and leaving all other parameters unchanged [6]. The values used were $r_0(\mathrm{C(aryl)}{-}\mathrm{C}(sp^3)) = 1.85$ and 2.12, and $r_0(\mathrm{C}(sp^3){-}\mathrm{C}(sp^3)) = 1.87$ and 2.15 for Si in II and Sn in III, respectively.

Full relaxation of idealized input structures of I, II and III led to similar ground state (GS) geometries for the three species. Figure 1 depicts two views of the GS of II. The gross distortions calculated may be summarised as: increase of the bond angles between atoms 9—1—11 and 9—8—12, opposite out-of-plane deflections of the two substituents, and distortion of each ring of the naphthalene nucleus to a half-chair with resultant near C_2 symmetry. Such distortions have been determined previously both for a substituted analogue of I by X-ray diffraction methods, and for I itself by EFF calculations using an alternative force field (MMPI) which allows explicitly for π-electron effects [7] ***,§.

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[*] This feature is the main weakness of this force field. However, we are concerned with trends, and believe that any errors will cancel across the series investigated. The consistency of the majority of the computed results with available experimental data leads us to accept the veracity of the model.

[**] The dihedral angle 7-8-12-16 was incremented in both directions and the coordinates of atoms 3, 6 and 16 were locked to prevent relaxation to ground state during further energy minimization.

[***] As might be expected the most serious discrepancy is the failure of our model to reproduce bond-length alternation in the naphthalene nucleus.

[§] Full atomic coordinates for structures of I, II and III are available on request.

[§§] We are aware of the inexactitude of comparing $E_{\max}$ (1) with experimental $\Delta G^{\neq}$. $\Delta G^{\neq}$ (—142°) = 6.5 kcal/mol for I [2].

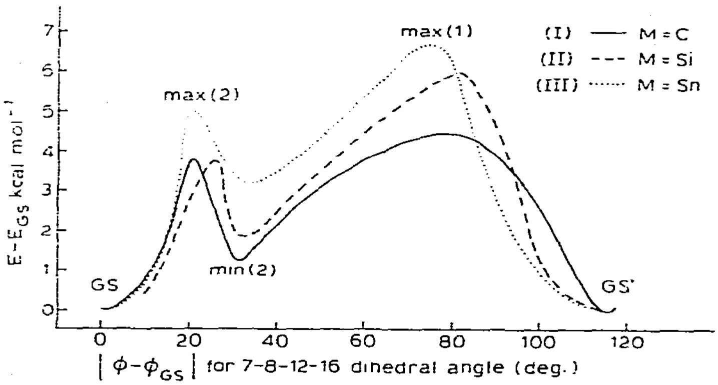

Fig. 2. Group driving experiments for I, II and III.

The group driving experiments also gave similar results for I, II and III, as shown in Fig. 2 and Table 1. The relative transition state energies ($E_{\max(1)}$) for I and III are consistent with the dnmr-derived $\Delta G^{\neq}$ values [1,2] §§, showing that our model can also reproduce dynamic properties of these molecules. On the basis of our calculations we predict that the energy ($E_{\max(1)}$) for the silicon compound II should lie between those of its carbon and tin analogues, I and III. EFF calculations on II using an alternative Si parameter set with a softer C—Si stretching force constant gave essentially identical results.

Each of I, II and III possesses a secondary minimum energy conformation (min (2)) of C_1 symmetry. As a consequence two energy maxima are traversed in one automerization (see Fig. 2). In all three cases max (2) corresponds to near eclipsing of the 8—9 bond by a methyl of the driven group, while the rate determining energy maximum (max (1)) has a methyl approximately eclipsing the 7—8 bond. During the rotation of one substituent, the other merely librates and no permutation of its three methyl groups is observed, i.e. no gearing or correlated rotation [8] occurs. Furthermore, rotation of a substituent does not

TABLE 1

Conformation		Compound		
		I	II	III
GS	E_{steric} (kcal mol^{-1})	30.85	6.36	4.07
	$\phi_{7\text{-}8\text{-}12\text{-}16}$ (degrees)	—43.0	32.6	86.2
	$\phi_{2\text{-}1\text{-}11\text{-}13}$ (degrees)	—42.8	31.0	89.4
max (2)	E_{steric} (kcal mol^{-1})	34.58	10.31	9.17
	$\phi_{7\text{-}8\text{-}12\text{-}16}$ (degrees;	—64.2	56.8	69.9
	$\phi_{2\text{-}1\text{-}11\text{-}13}$ (degrees)	—51.6	44.6	52.4
min (2)	E_{steric} (kcal mol^{-1})	32.19	7.93	7.08
	$\phi_{7\text{-}3\text{-}12\text{-}16}$ (degrees)	—73.8	65.0	51.8
	$\phi_{2\text{-}1\text{-}11\text{-}13}$ (degrees)	—63.7	63.3	54.5
max (1)	E_{steric} (kcal mol^{-1})	35.52	12.39	10.98
	$\phi_{7\text{-}8\text{-}12\text{-}16}$ (degrees)	—121.5	112.2	12.5
	$\phi_{2\text{-}1\text{-}11\text{-}13}$ (degrees)	—57.0	53.1	65.8

effect enantiomerization of the molecule, consistent with the experimentally derived barrier of greater than 24 kcal/mol for enantiomerization of I [2]. The absence of correlated rotation and enantiomerization during t-butyl rotation has also been noted by Hounshell and Mislow [9] in related investigations.

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