Molecular Structures Determined by Intramolecular Attractive Steric Interactions. Dynamic NMR and Molecular Mechanics Investigation of 1,6-Dimethylcyclo-octatetraene

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1,6-Dimethylcyclo-octatetraene equilibrates with 1,4-dimethylcyclo-octatetraene by a bond-shift process which is slow on the NMR timescale at ambient temperature. The greater stability of the former valence isomer ($\Delta G_0 = 0.081$ kcal mol^{-1}† at 20 °C in perdeuteriobenzene solution) is attributed to attractive steric interaction between methyl groups. NMR spectra of the equilibrium mixture are considered in detail with a view to characterising other 1,6 ⇌ 1,4-disubstituted cyclo-octatetraene equilibria. Diagnostically useful differences in spectra are demonstrated, while some apparently clear differences are due to second-order effects. Molecular mechanics calculations agree with experimental results as to the preferred valence isomer and confirm that it has greater methyl–methyl attractive steric interactions. There are three slightly different conformations present in similar relative amounts for each valence isomer due to methyl rotation, and NMR results do not disagree with this suggestion.

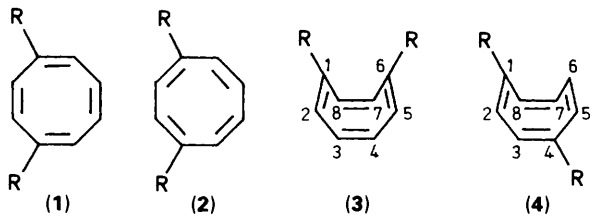
Attractive steric interactions within molecules are much more common than repulsive ones yet have received much less attention in the history of conformational analysis.[1] In all but the smallest molecules, most pairs of atoms will be separated by more than the sum of their van der Waals radii, *i.e.* beyond repulsion, but the contribution to the enthalpy of the molecule of the few atoms interacting repulsively will usually be greater, often much greater, than the stabilisation from attractive steric interactions. The maximum value of any single pairwise attraction is likely to be about 0.05 kcal mol^{-1}.

The most elusive aspect of attractive steric interactions is the stabilisation produced by the interaction of two saturated hydrocarbon fragments too distant to repel each other. In the limiting case where both fragments are non-polar there remains a weak induced dipole/induced dipole interaction (weak, as carbon–carbon and carbon–hydrogen bonds in saturated fragments are not very polarisable). Practically, however, this will be enhanced by the weak polarity of the first fragment (weak, as there are no large differences in atom electronegativity) interacting with the weak polarity or polarisability of the second.

In view of the dominating omnipresence of repulsive interactions, one tactic for studying attractive steric interactions is to devise and study molecules for which there are two similar structures in both of which the repulsive steric interactions are the same, but which have different attractive interactions.[1]

It has recently been shown that 1,6-disubstituted cyclo-octatetraenes (**1**) equilibrate with the 1,4-isomers (**2**) by a bond-shift process slow enough on the NMR timescale to allow direct measurement of the populations of the two states.[2,3] The cyclo-octatetraene conformation is tub-shaped and the immediate environment of each group R in both forms is the same, the only difference appearing to be whether the groups R are near to each other as in the 1,6-isomer (**3**), or further away as in the 1,4-isomer (**4**). For the di-t-butylcompounds,[2] the 1,6-isomer (**3a**) with the t-butyl groups close together in space is more stable than the 1,4-isomer (**4a**), the ratio of populations being 2.08 at 25 °C in deuteriochloroform solution, representing a free energy difference of 0.43 kcal mol^{-1} in favour of (**3a**).

Molecular mechanics calculations[4,5] satisfactorily reproduce the (**3a**), (**4a**) energy difference as do *ab initio* calculations, as long as the latter[5] are carried out without approximations



a; R = $C(CH_3)_3$
b; R = CH_3
c; R = CD_3

which preclude electron correlation between pairs of atoms, *i.e.* attractive steric interactions. Calculations have also been carried out[4,5] on corresponding dimethylcyclo-octatetraenes (**1b**) and (**2b**) and suggest that in this case as well, the 1,6-isomer should be slightly more stable than the 1,4-isomer by 0.02 kcal mol^{-1}. This pair of compounds has been prepared previously, presumably as a mixture[6] but the equilibrium has not been studied.

We feel that the subject of attractive steric interactions deserves greater investigation not only for itself but also as an intramolecular model for lipophilic interaction, and that the (**1**) ⇌ (**2**) equilibrium is a good basis for a systematic study. In simpler examples than the di-t-butyl set, coupling between the substituent and the ring protons should give detailed information on the interaction between groups and the differences between group conformations.

This has been shown to be the case, and we want now to give a detailed account of the (**1b**) ⇌ (**2b**) equilibrium, showing the extent of the information that is available from careful NMR work, supported by molecular mechanics calculations.

Results

NMR Spectra.—The (**3b**) ⇌ (**4b**) equilibrium mixture was synthesized by the method of Paquette and co-workers[6] exploit-

† 1 cal = 4.184 J.

Table 1. ^{1}H Chemical shifts[a] and relaxation times[b] (T_1/s) at 20° and −32° for (**3b**) ⇌ (**4b**).

	Methyl group			H_2, H_3			H_7, H_8		
	Shift	T_1[c]	T_1[d]	Shift	T_1[c]	T_1[d]	Shift	T_1[c]	T_1[d]
(**3b**) 1,6-isomer	1.609	2.59	1.33	5.15, 5.73	4.73	2.61	5.63	4.54	2.51
(**4b**) 1,4-isomer	1.626	2.53	1.27	5.54	4.48	2.45	5.67, 5.70	4.54	2.58

[a] C_6D_6 solution. [b] $CDCl_3$ solution. [c] At 20 °C. [d] At −32 °C.

Table 2. ^{13}C Chemical shifts and relaxation times (T_1/s) for $CDCl_3$ solution of (**3b**) ⇌ (**4b**).

	Methyl group		Methine carbons						C–carbon	
	Shift	T_1	Shift	T_1	Shift	T_1	Shift	T_1	Shift	T_1
(**3b**) 1,6-isomer	23.76	5.02	126.44	6.22	131.22	6.07	133.24	6.40	140.12	30.27
(**4b**) 1,4-isomer	23.50	5.33	127.09	6.47	130.03	6.25	134.97	5.93	138.94	32.67

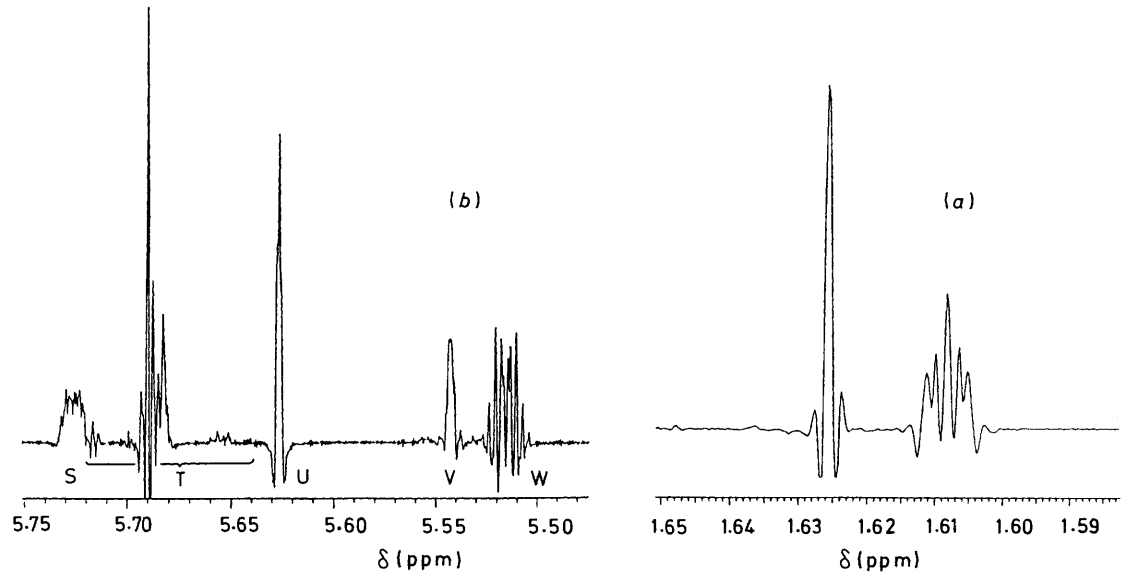


Figure 1. ^{1}H NMR spectra of a perdeuteriobenzene solution of the (**3b**) ⇌ (**4b**) mixture. (*a*) Methyl region; (*b*) alkene region. S,W = H2–H5; U = H7, H8 in (**3b**); V = H2, H3, T = H5–H8 in (**4b**), X,Y = methyl in (**4b**) and (**3b**), respectively.

ing Huisgen's synthesis of cyclo-octatetraene-1,4-sulphone.[7] The 400 MHz proton NMR spectrum for a perdeuteriobenzene solution is shown in Figure 1(*a*) for the methyl protons, and in Figure 1(*b*) for the alkenic protons, and comprises two subspectra in the intensity ratio (**3b**):(**4b**) 1.15:1, determined from various signals by various integration methods, see the Experimental section. From this ratio, the relative enthalpy of the two isomers is 81 cal mol^{-1} at 20 °C, if their entropies are the same. The assignment of peaks is as indicated in the Figure, and is based on the reliable premise that in the 1,4-isomer non-identical adjacent protons [7 and 8 in (**4b**)], will have a coupling constant of about 11 Hz, a vicinal coupling *cis* on a double bond, while in the 1,6-isomer the corresponding coupling constant (between non-identical adjacent protons 2 and 3) will be about 3 Hz, a vicinal coupling along a single bond where the dihedral angle is 45–50° according to molecular mechanics calculations. Table 1 gives details of the spectra.

Two sets of subspectra of different intensity are seen in the ^{13}C NMR spectrum of (**1b**) + (**2b**). Table 2 has details while Figure 2 shows the methyl region of the spectrum without proton decoupling.

NMR spectra are solvent dependent to the extent that some relative chemical shifts change sign, but the position of the (**3b**) ⇌ (**4b**) equilibrium does not seem to change. Similar observations have been described less unequivocally for the (**3a**) ⇌ (**4a**) equilibrium.[6]

On raising the temperature of a DMSO solution, all signals broaden up to about 52 °C at 200 MHz when signals merge. On further heating signals sharpen until a single average spectrum is obtained for the (**3b**) ⇌ (**4b**) mixture, indicating that the bond shift has become rapid on the NMR timescale. All changes are reversed on return to room temperature. At the coalescence temperature the barrier to the interconversion is calculated to be 17.3 kcal mol^{-1}.

Molecular Mechanics Calculations.—Calculations for bond shift-isomers (**1b**) and (**2b**) have been reported elsewhere.[4] We have repeated these in rather more detail with respect to the methyl groups' rotational conformations which are undoubtedly significant but which were not considered in that earlier report.

There are two stable conformations for a methyl group, separated by 60° of rotation, depending on whether a proton is antiperiplanar (**5**) or synperiplanar (**6**) with respect to the double bond, and the former is calculated to be more stable by

Table 3. Molecular mechanics calculations of the three conformations, *anti, anti*; *anti, syn*; and *syn, syn* of (**3b**) and (**3b**), enthalpies in kcal mol^{-1}

	anti, anti		*anti, syn*		*syn, syn*	
	1,6-isomer (**3b**)	1,4-isomer (**4b**)	1,6-isomer (**3b**)	1,4-isomer (**4b**)	1,6-isomer (**3b**)	1,4-isomer (**4b**)
Methyl-1 dihedral angle[a]	−172.1	−179.6	−172.7	−179.7	−2.0	−4.1
Methyl-4(6) dihedral angle	171.8	−179.6	1.5	−3.5	3.2	−4.1
Total steric energy	10.3742	10.4253	10.6420	10.6798	10.8946	10.9322
Compression[b]	0.1784	0.1800	0.1860	0.1927	0.1950	0.2053
Bond angle bending	2.1514	2.2018	2.2365	2.2584	2.3059	2.3140
Stretch-bend	0.0366	0.0345	0.0388	0.0375	0.0411	0.0403
van der Walls 1,4-energy	4.4016	4.3988	4.2986	4.3067	4.2050	4.2186
van der Waals longer-range energy[c]	−1.7460	−1.7615	−1.5406	−1.5026	−1.3233	−1.2418
Torsional strain	5.3332	5.3561	5.4035	5.3716	5.4518	5.3802
Dipolar	0.0191	0.0155	0.0192	0.0155	0.0192	0.0155
Sum of 16 pairwise methyl atom interactions	−0.0898	−0.0223	−0.0967	−0.0223	−0.1059	−0.0222

[a] Angle in °. For *syn* and *anti* methyl groups dihedral angles reported are for the hydrogen nearly eclipsing the double bond and nearly antiperiplanar to the double bond, respectively. Values are never exactly 0 and 180°, and in every case the sign tells that rotation has taken the hydrogen to a position outside perfectly periplanar rather than inside. [b] Strain energy from lengthening or shortening bonds. [c] The negative sign indicates stabilisation rather than strain.

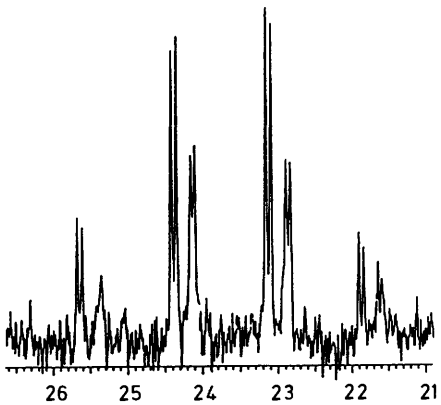
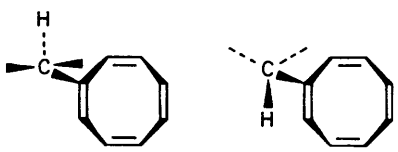


Figure 2. Methyl region of the ^{13}C NMR spectrum of the (**1b**) ⇌ (**2b**) mixture in deuteriobenzene solution at 20 °C.

about 0.26 kcal mol^{-1}. For both dimethylcyclo-octatetraenes there are thus three different conformations, *anti, anti*; *anti, syn*; and *syn, syn*. The calculated enthalpies of these are shown in Table 3, and in each case the 1,6-dimethyl compound is more



(**5**) (**6**)

stable than the 1,4 compound by 38–51 cal mol^{-1}. The Table shows the various contributions to the total enthalpy of the two isomers and the sum of the sixteen pairwise atomic interactions of the two methyl groups for each conformation.

The difference between bond-shift isomers is thus much smaller than the difference between methyl group conformations within each isomer but the conformational behaviour of the two compounds is parallel within the limits of reproducibility of molecular mechanics minimisation. Each compound should exist as a very similarly composed mixture of all conformations *viz.*, 37% *anti, anti*, 24% each of *anti, syn* and *syn, anti*, and 15% of *syn, syn*. The conformationally weighted enthalpy difference is calculated to be 43 cal mol^{-1} whence the relative amounts of the two valence isomers is calculated to be 1.076:1 in satisfactory agreement with the experimental observation of 1.15:1.

Discussion

The (**3b**) ⇌ (**4b**) *Equilibrium.*—Molecular mechanics calculations predict and NMR observations confirm that (**3b**) is more stable than (**4b**) by 43 and 81 cal mol^{-1} respectively. The molecular mechanics comparison focuses on very small differences between large quantities, where the difference between isomers is much smaller than conformational differences within isomers. The justification for seeing significance in the results is that the experimental one is incontrovertible and in agreement with the calculations. With more highly substituted analogues of (**1**) and (**2**), the effects will be greater, yet discussion of spectra, of conformations, and of energy differences will inevitably be in terms similar to those used now. It is gratifying that calculations and experiment agree as to the sense of the stability and the order of magnitude.

A feature of the calculations which should not be ignored when attaching significance to small enthalpy differences is that of reminimisation discrepancies. Minimum energy co-ordinates when resubmitted to the program as starting co-ordinates may, and in the present case do, lead to slightly different minimum energies which vary randomly if the process is repeated several times. This probably reflects the finite size of the improvement cut-off point and other approximations in the minimisation procedure. In the case of the *anti, anti* conformation of the two isomers the range of minimum energies was found to be 9 cal mol^{-1} over six reminimisations.

Such a reminimisation discrepancy contrasts with our experience in polycyclic compounds such as adamantane derivatives where successive reminimisations lead by minute steps to increasingly stable structures. This may be associated with the greater interdependence of parameters in the polycyclic structure compared with a more open one.

The (**3b**) ⇌ (**4b**) equilibrium as measured by the ratio of peak intensities is not significantly temperature dependent over the range that could be measured, −50 °C to +40 °C. It thus seems that there is a true enthalpy difference favouring the 1,6-isomer, and the entropies of the two isomers are the same within experimental error. The 1,6-isomer might have lower entropy since the methyl groups interact, and might thus restrict each other, but the results do not indicate this.

This contrasts with the observation of Streitwieser and his

Table 4. Barriers to bond-shift in substituted cyclo-octatetraenes.

Substituents	Barrier, G^+, kcal mol^{-1} and (temperature, K)	Reference
None	13.7 (263)	8
1-OCH_3	16.4 (273)	9
1,2-$(CH_3)_2$	21.1 (395)	10
1,2,3-$(CH_3)_3$	26.8 (363)	11
1,2,3,4-$(CH_3)_4$	33.7 (433)	11
1,4- and 1,6-$(Bu^t)_2$	22.6 (298)	2
1,4- and 1,6-$(CH_3)_2$	17.3 (325)	This work

colleagues[2] on the (**3a**) $\rightleftharpoons$ (**4a**) equilibrium which showed a temperature dependence of the equilibrium which led to enthalpy and entropy differences of 0.489 kcal mol^{-1} and 0.92 eu,* respectively. Paquette[3] and his co-workers were not able to confirm this temperature dependence.

The molecular mechanics calculations predict differences in many terms as contributing in different senses to the overall relative stability of (**3b**) compared with (**4b**). This suggests caution in assigning the stability of (**3b**) to attractive steric interactions. However, molecular mechanics reports all the adjustments the molecule makes to lower its total enthalpy including increasing other kinds of strain when this leads to an even greater increase in attractive interactions. We therefore extracted and summed the sixteen pairwise interactions between methyl group atoms in the various conformations of the structures (**3b**) and (**4b**), see Table 3, and these sums, between 67 and 84 cal mol^{-1} always favouring (**3b**), emphasize the importance of these interactions.

Table 4 lists the barriers to bond shift in substituted cyclo-octatetraenes. There is a well-defined trend to higher barriers with increased number, size, and relative proximity of substituents, into which the present result, a barrier of 17.3 kcal mol^{-1} to interconversion of (**3b**) and (**4b**), fits. In a planar or near-to-planar transition state, interaction of substituents along what were originally single bonds must be greatly increased, and this can be expected to be the main source of substituent effects on the barrier.

NMR Spectra.—The calculations do not predict significantly different mixtures of conformations about the methyl to cyclo-octatetraene bond for the two isomers. NMR spectra of the isomers, on the other hand, show different coupling patterns between methyl groups and the rest of the molecule, see Figures 1 and 2, but these do not reflect different methyl-group conformations, but rather differing complexity of coupling pathways.[12]

The signals U and V in Figure 1(*b*) are assigned to the isolated identical alkenic protons at the 7,8-position in (**3b**) and the 2,3-position in (**4b**) respectively. These have weakly resolved splitting of about 0.5 Hz magnitude, shown by double-irradiation experiments to represent coupling with the adjacent methyl group. The *cis*-proton to methyl-proton coupling in propene is 1.27 Hz.[13] In both U and V the splitting is less than the coupling constant since an isolated proton is coupled in a different way, with opposite sign, to each of the methyl groups. Furthermore, the different ways are not the same in (**3b**) and (**4b**), where the identical isolated protons are linked by a double bond and by a single bond, respectively. The differing appearance of the methyl signals in the proton NMR, see Figure 1(*a*), is explained similarly.

Signal T in Figure 1(*b*) is an AA'BB' spectrum for protons 5–8 in (**4b**) where an AB coupling of about 11 Hz can be distinguished. Decoupling the appropriate methyl signal at δ 1.626 (which shows little structure), has only a small effect on T, and the decoupled spectrum can be simulated as an AA'BB' spectrum with J_{AB} 11.1 and $J_{AB'}$ 3.5 Hz. Again the apparent absence of coupling of A and B to the methyl groups reflects the opposite sign of these couplings, the near coincidence of the A and B chemical shifts and the large AB coupling constant.

Signals S and W in Figure 1(*b*) make up the AA'BB' spectrum for protons 2–5 in (**3b**), where A and B have a large relative chemical shift equivalent to 84 Hz at 400 MHz and are weakly coupled, J_{AB} 3.0 Hz. This coupling emerges from decoupling the methyl group at δ 1.627 and spectral simulation, as do couplings of A and B to the methyl group of 1.3 and 0.6 Hz respectively, quite usual values.[13]

We expect that the difference in the AA'BB' spectra due to protons 2–5 in (**3b**) and 5–8 in (**4b**) will be diagnostic of the 1,6- and 1,4-isomers respectively. These are chemically quite different AA'BB' systems so such spectral differences are to be expected.

Turning to the ^{13}C NMR spectrum of the compounds (**3b**) and (**4b**), chemical shifts, although clearly different, deserve only a little comment. The methyl groups in (**3b**) are attracting each other, and may have a different rotational conformation from those in (**4b**). Whether either of these explanations will prove to be a characteristic explanation of the downfield displacement of the methyl and C-1 shift in (**3b**) compared with (**4b**), remains to be seen.

Differences between ^1H–^{13}C coupling constants for (**3b**) and (**4b**) are expected to be more significant. The one bond coupling constant of the methyl carbon is the same within experimental error, 126.7 and 126.4 Hz for (**3b**) and (**4b**), respectively. There is, however, a significant difference in the *cis* vicinal coupling of the methyl carbon to the vinylic proton in the two isomers, 6.8 ± 0.2 Hz in the major isomer (**3b**), and 5.5 ± 0.3 Hz for the minor isomer (**4b**). The question arises again whether this reflects a change in methyl group conformation between isomers, but a consideration of structures (**3**) and (**4**) and spectral simulation show that this need not be so. 3-H in (**4**) is identical with 2-H, so the first-order analysis of the ^{13}C spectrum which can be used for the 1,6 isomer (**3**), is no longer appropriate for (**4**). Rather, the coupling of 3-H with the methyl carbon, reasonably of opposite sign to that of 2-H means that the doublet splitting is the algebraic sum of these two coupling constants. The heights of the two quartets (see Figure 2) are in a ratio different from the signal intensity ratio of 1.51:1, confirming the complex nature of the apparent doublets of the minor isomer. Spectral quality is too low to justify further study of this point.

The question arises as to whether nuclear spin relaxation times are different in the isomers, *i.e.* whether they are affected by the postulated attractive steric interactions. Results are shown in Tables 1 and 2 and show no significant differences. Determination of spin–lattice relaxation times T_1 at room temperature is complicated by the fact that although interconversion of the two isomers is slow on the NMR timescale, it is not slow on the relaxation timescale, that is, the half-life for valence isomerism is comparable to relaxation times. Proton relaxation times T_1 were therefore also determined at − 32 °C, see Table 1, but no significant differences emerged at this temperature either.

We exploited the similarity in rates of valence isomerisation and nuclear spin relaxation at room temperature to carry out a saturation transfer measure of the valence isomerisation rate.[14] Pre-irradiation of a signal from one isomer leads to saturation of the corresponding signal of the other isomer, which appears as a decrease in the intensity of that signal, depending on the pre-irradiation time and the rate constant for valence isomerisation. By this means we measured a

* 1 eu = 4.184 J K^{-1} mol^{-1}.

rate-constant of 0.58 s^{-1} for interconversion of (**3b**) $\rightleftharpoons$ (**4b**) at 20 °C which leads to a free energy of activation for valence isomerisation of 17.48 kcal mol^{-1} at 20 °C, in good agreement with the value of 17.3 kcal mol^{-1} at 52 °C found from the coalescence of the signal.

We also investigated the bond-shift equilibrium for the isomers (**3c**) and (**4c**) with two trideutieriomethyl groups. The appearance of the alkene region was very similar to the parent spectrum with decoupling at the methyl proton signals. The fractional populations of the two isomers were the same as for the protio series within experimental error.

Experimental

The mixture of (**3b**) and (**4b**) was prepared according to the method of Paquette and co-workers.[6] Compounds (**3c**) and (**4c**) were prepared similarly using deuteriated methyl iodide at the alkylation stage.

NMR spectra were recorded using a Varian VXR400 spectrometer operating at 400 MHz for protons and 100.6 MHz for carbon. Relative intensities of signals were determined from ^1H NMR spectra using the spectrometer's electronic signal integrator, and by planimetry of plotted signals. Care was taken to avoid saturation effects. In various solvents, using various signals, at various temperatures, slight variations in the (**3b**):(**4b**) equilibrium constant were measured, none of which were systematic enough to indicate a solvent or temperature effect on the equilibrium. All measured equilibrium constants fell within the range (1.23 ± 0.11):1 whence a free energy difference of 121 ± 56 cal mol^{-1} at 20 °C can be calculated. Molecular-mechanics calculations were carried out using Allinger's MMP282 program.[15]

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