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Electron-Diffraction Investigations of the Molecular Structures of *cis*- and *trans*-1,2-Dimethyldiborane

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Abstract: The structures of *cis*- and *trans*-1,2-dimethyldiborane have been investigated at room temperature by gas-phase electron diffraction. The more important distances (r_a/Å), angles (∠/deg), and amplitudes of vibrations (l/Å), with uncertainties estimated at 2σ, are as follows: r(B–B) = 1.798 (7) (cis), 1.799 (8) (trans); r(B–C) = 1.579 (2), 1.581 (3); r(B–H$_b$) = 1.358 (6), 1.365 (8); r(B–H$_t$) = 1.239 (8), 1.241 (10); r(C–H) = 1.108 (2), 1.110 (3); ∠BBC = 122.6 (5), 121.8 (6); ∠BBH$_t$ = 117.0 (assumed), 118.5 (27); ∠BHC = 113.3 (2.1), 112.5 (2.6); l(B–B) = l(B–C) + 0.0100 = 0.0726 (32), 0.0721 (33); l(B–H$_b$) = l(B–H$_t$) + 0.0140 = l(C–H) + 0.0600 = 0.0865 (40), 0.0891 (44). The contribution of H distances dependent on methyl torsion was described in terms of cosinusoidal one-methyl potential functions, both threefold and sixfold for the cis (V_3 = 1.5 kcal/mol, lowest for CH_3 staggered to $B(H_b)_2H_t$; $V_6 = -0.5$ kcal/mol) but only threefold for the trans (V_3 = 2.0 kcal/mol). The distance and angle values generally lie between those of diborane and tetramethyldiborane, and it seems that there is appreciable methyl–methyl repulsion in the cis compound.

The isolation and characterization of the two stereoisomers of 1,2-dimethyldiborane(6)[2] (DMDB) afforded the opportunity to establish the molecular structures quantitatively and to make comparisons with diborane(6)[3] and some of its other derivatives. The indications were of little change in dimensions in the remnant of the parent molecule[4] except on extensive substitution to tetramethyldiborane(6) (TeMDB), which considerably lengthens the B–B distances.[5a] The B–C distance, however, remains nearly the same in TeMDB, and even in trimethylborane,[5b] as it is in monomethyldiborane(6)[4a] (MMDB).

Experimental Section

Samples of *trans*-1,2-DMDB (93%, mp −102 °C) and *cis*-DMDB (96%, mp −132.5 °C) were purified at the University of Washington and transported at −196 °C to Oregon State University in sealed Pyrex tubes. For the diffraction experiments they were warmed to −70 to −65 °C to provide vapor pressures of about 15 Torr. About 3 mmol of each was used. The remainder of each sample was reassayed, and no detectable change in purity was found in either.

Diffraction photographs were made in the Oregon State apparatus, with an r^3 sector and 8 × 10 in. Kodak projector slide (medium) plates at nominal nozzle-to-plate distances of 70 and 30 cm (long and intermediate cameras). Other experimental conditions: nozzle tip at room temperature for trans and at −27 °C for cis; beam currents, 0.4–0.5 μA; exposure times, 1.5–3.0 min; ambient apparatus pressure during exposures, $0.6\text{–}2.0 \times 10^{-5}$ Torr; plate development, 10 min in D-19 diluted 1:1; electron wavelengths about 0.057 Å determined by a voltage measurement, calibrated in separate experiments with gaseous CO_2 (r_a(C=O) = 1.164 Å and r_a(O⋯O) = 2.3244 Å).

The plates (cis, three long camera and four intermediate camera; trans, three long and two intermediate) were handled as described previously[6] to obtain scattered intensity data. Calculated, smooth backgrounds[7] containing contributions from theoretical elastic[8] and inelastic[9] electron scattering amplitudes were subtracted to give the molecular intensity distributions (Figure 1), for these molecules adequately represented by

$$sI_m(s) = k \sum_{i,j} A_iA_jr_{ij}^{-1}\exp(-l_{ij}^2s^2/2)\cos(\eta_i - \eta_j)\sin r_{ij}s \qquad (1)$$

The ranges of the data from the long and intermediate camera distances were $2.00 \leq s \leq 12.75$ Å^{-1} and $7.00 \leq s \leq 31.00$ Å^{-1} for cis and $1.00 \leq s \leq 12.75$ Å^{-1} and $7.00 \leq s \leq 31.50$ Å^{-1} for trans; the data interval was $\Delta s = 0.25$ Å^{-1}. The reduced data, calculated backgrounds, and molecular intensity averages are available as supplementary material.

The least-squares structure refinements[10] were based on eq 1 with A's and η's derived[11] from tables.[8] The observed intensity data were

0002-7863/80/1502-3430$01.00/0

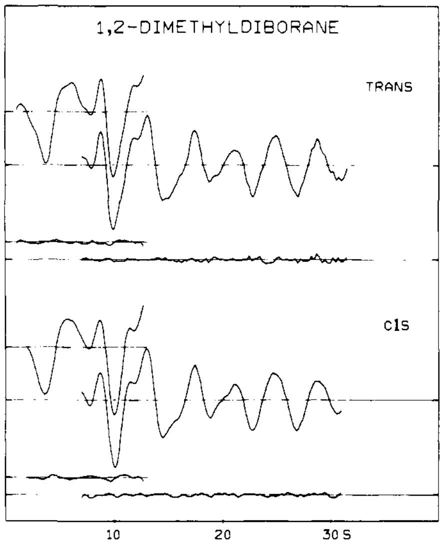

Figure 1. Experimental molecular intensity curves. The upper pairs for each molecule are the averages of $sI_m(s)$ from the long and intermediate cameras; the lower pairs are the differences between these and the intensities calculated for the models of Table 1.

formed into averages from each camera distance to give two data sets for each molecule; each refinement adjusted to these sets simultaneously. Radial distribution curves were calculated in the usual way after multiplication of the $sI_m(s)$ curves by $Z_BZ_C(A_BA_C)^{-1}$ $\exp(-0.0025)s^2$. The experimental radial distribution curves were calculated from composites of the two average $sI_m(s)$ curves using a theoretical intensity curve for the unobserved region $s < 2.00$ Å^{-1}.

Structure Analysis

The experimental radial distribution curves for the two molecules (Figure 2) immediately revealed their isomeric identities: the peak at ~4.4 Å in the upper curve has substantial weight and can correspond only to a trans carbon-carbon distance. The important remaining peaks of each curve were also easily assigned as indicated by the labels on the vertical bars. Figure 3 shows the atomic arrangements in the molecules.

The symmetries of the two molecules were assumed to be C_{2h} (trans) and C_{2v} (cis) exclusive of methyl-group rotation. Other simplifying assumptions included planarity of the four-membered ring and local C_{3v} symmetry for the BCH_3 groups. (These assumptions were tested in late refinements and found to be fully appropriate.) If one disregards the methyl-group torsion angles, the shapes of the molecules are determined by values of r(B-B), r(B-C), r(B-H$_b$), r(B-H$_t$), r(C-H), ∠BBC, ∠BBH$_t$, and ∠BCH. Each distance in each molecule has an associated vibrational amplitude. Disregarding all distances affected by methyl-group torsion as well as $H_t \cdots H_t$ these number 15 each, too many for independent refinement. This number was reduced to eight by forming the group-amplitude parameters evident from Table I. The amplitude differences within a group were estimated from experience and maintained during the cycling.

As the work proceeded, it became clear that methyl-group torsion in the two molecules was an important parameter, at least in a differential sense. The observation was that the good fit provided by a trans molecule with methyl groups staggered with respect to the adjacent BH_3 part and oscillating harmonically could not be duplicated for the cis molecule. Further investigation suggested that methyl-group rotation is less restricted in the cis than in the trans isomer and that a more elaborate approach was required to expose the differences. This approach, which has been successfully used in studies of methyl-group torsions in 2,3-dimethylbutadiene[12] and in the

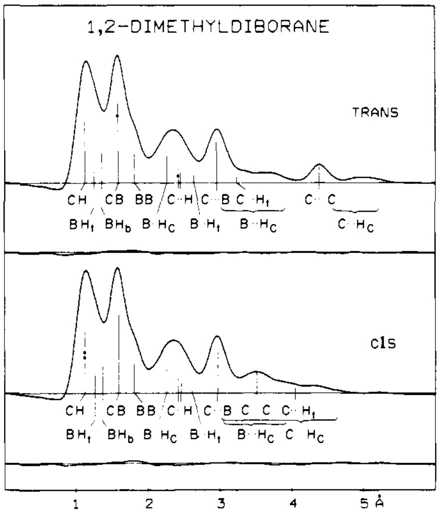

Figure 2. Experimental radial distribution curves. The vertical lines correspond to the distances of Table I; their lengths are proportional to the weights of the terms. The differences experimental minus theoretical are shown below each curve.

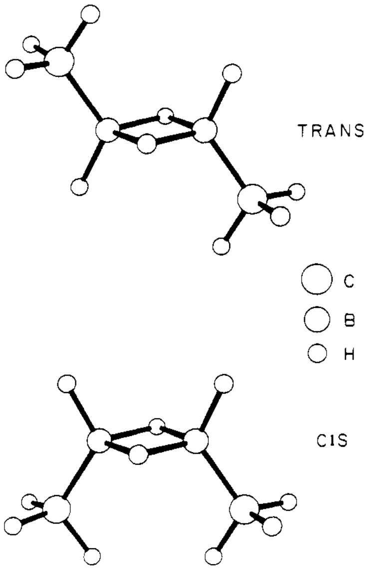

Figure 3. Model diagrams for *cis*- and *trans*-1,2-dimethyldiborane.

trimethylphosphine and arsine oxides and sulfides,[13] comprises simulation of the three rotating hydrogen atoms with 12 ¼-hydrogens distributed at 30° intervals on the circle of rotation each weighted according to its angular position by the Boltzmann factor $Q^{-1}\exp[-V(\phi)/RT]$. We chose the potential function

$$2V(\phi) = V_3(1 - \cos 3\phi) + V_6(1 - \cos 6\phi) \qquad (2)$$

with $\phi = 0°$ defined as the staggered conformation of the methyl and BH_3 parts. The torsional problem was then explored for the cis molecule in a series of refinements differing only in the values assigned to V_3 and V_6. For the trans molecule it was sufficient to set V_6 equal to zero and to vary only V_3.

The results are presented in Tables I (the best models) and II (correlation matrices for the more important parameters) and Figures 1 and 2 (intensity and radial distribution curves). The final refinements leading to these results included all terms except H···H through two or more bond angles. Shrinkage corrections were ignored. Parentheses denote assumed values, judged unrefinable, except for V_3 and V_6, which were fixed as described above and are probably subject to 2σ uncertainties of at least 1 kcal mol^{-1}.

Table I. Structural Results from the Least-Squares Refinements for *cis*- and *trans*-1,2-Dimethyldiborane[a]

	cis-				*trans*-			
	r_a, θ, V	2σ	l	2σ	r_a, θ, V	2σ	l	2σ
B–B	1.798	0.007	0.0726	0.0032	1.799	0.008	0.0721	0.0033
B–C	1.579	0.002	0.0626		1.581	0.003	0.0621	
B–H_b	1.358	0.006	0.0865		1.365	0.008	0.0891	
B–H_t	1.239	0.008	0.0725	0.0040	1.241	0.010	0.0751	0.0044
C–H	1.108	0.002	0.0805		1.110	0.003	0.0831	
∠BBC	122.6	0.5			121.8	0.6		
∠BBH_t	(117.0)				118.5	2.7		
∠BCH	113.3	2.1			112.5	2.6		
V_3	(1.5)				(2.0)			
V_6	(−0.5)				(0.0)			
%[b]	91	10			83	15		
B·C	2.964	0.004	0.0906	0.0049	2.956	0.006	0.0990	0.0060
C··C	3.500	0.017	0.1559	0.0232	4.386	0.009	0.0901	0.0144
C·H_b	2.422	0.006	0.1446		2.422	0.007	0.1490	
C·H_t	2.453	0.009	0.1646	0.0145	2.446	0.038	0.1690	0.0191
B·H_C	2.259	0.025	0.1646		2.254	0.032	0.1690	
B·H_t	2.606	0.009	0.1646		2.628	0.037	0.1690	
C··H_t	4.030	0.009	(0.1700)		3.235	0.057	(0.1500)	
H·H[c]	1.76–2.10	0.03	0.1056	0.0214	1.78–2.11	0.04	0.0995	0.0193
B··H_C	3.03–3.92	0.04	0.24–0.15	0.08	3.00–3.90	0.05	0.21–0.12	0.04
C···H_C	3.02–4.60	0.04	0.24–0.12	0.08	4.57–5.21	0.05	0.24–0.18	0.08
R[d]	0.0534				0.0667			

[a] Distances (r) and amplitudes (l) in angstroms; angles (θ) in degrees; rotational barriers (V) in kcal/mol. Parenthesized values were assumed; bracketed quantities were refined as a group with constant differences within the group. In parameter labels one and two dots indicate geminal and vicinal distances, respectively. [b] The second isomer was trans in the case of the cis experiment and cis in the case of the trans. [c] These geminal distances include $H_b·H_b$, $H_b·H_t$, and $H_C·H_C$. [d] $R = [\Sigma_i w_i \Delta_i^2/\Sigma_i w_i s_i^2 I_i(\text{obsd})^2]^{1/2}$ with $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd})$.

Table II. Correlation Matrices (×100) for *cis*- and *trans*-1,2-Dimethyldiborane

	r(B–B)	r(B–C)	r(B–H_b)	r(B–H_t)	r(C–H)	∠BBH	∠BBC	∠BCH	l(B,C–H)	l(B,C–B)	l(B·C)	l(C,B·H)
						cis-						
σ[a]	0.0023	0.0006	0.0022	0.0026	0.0007		0.1657	0.7578	0.0007	0.0004	0.0012	0.0046
	100	−15	−12	0	−16		−85	56	−1	32	5	34
		100	62	24	34		0	−57	36	−5	14	−45
			100	39	60		1	−50	31	3	20	−38
				100	40		1	−25	10	34	25	−15
					100		10	−25	18	1	13	−13
							100	−47	−1	−22	−8	−27
								100	−36	−1	21	82
									100	28	23	−22
										100	28	5
											100	−19
												100
						trans-						
σ[a]	0.0028	0.0007	0.0028	0.0034	0.0009	0.9605	0.1971	0.9333	0.0009	0.0005	0.0016	0.0063
	100	−21	−27	−16	−25	42	−69	67	−8	25	−11	50
		100	66	28	38	−29	−10	−58	34	−4	19	−46
			100	41	62	−32	1	−55	27	2	21	−41
				100	39	−27	6	34	5	31	28	−22
					100	−17	10	−31	18	1	15	−18
						100	8	56	−20	−5	−20	59
							100	−34	−4	−17	0	−13
								100	−34	−4	−33	84
									100	29	24	−21
										100	27	3
											100	−30
												100

[a] Standard deviations from least squares. Distances and amplitudes in ångstroms, angles in degrees.

The composition parameter was introduced to take account of the other isomer present in each sample. To simplify the calculations the structure of the impurity substance was assumed to be that of the major component except for the configuration of the CBBC chain. The relatively small amount of impurity and the only very small differences between the short-range structures of the isomers ensure that this approximation can have no significant effect on the results. The least-squares estimates of isomer impurity are much larger than those determined by analysis, but not by more than the least-squares values of 2σ. We believe that the differences are probably real, and that they represent isomerization, which may have occurred in the necessarily long metal inlet tube (25 cm). In the earliest exposures (trans) it was inexpedient to cool the inlet tube, but in the later exposures (cis) some cooling was accomplished. This difference seems to be reflected in the two least-squares results of 83 ± 15 and 91 ± 10%.

The rather considerable difference in R value for cis and

Table III. Comparison of Some Borane Structures[a,b]

	DB[c]	MMDB[d]	*trans*-DMDB	*cis*DMDB	TeMDB[e]	TMB[f]
B–B	1.775(4)	1.773(5)	1.799(8)	1.798(7)	1.840(10)	
B–C		1.59[g]	1.581(3)	1.579(2)	1.590(3)	1.578(1)
B–H$_b$	1.339(4)	1.333(8)[h]	1.365(8)	1.358(6)	1.364(45)	
B–H$_t$	1.196(7)	(1.19)	1.241(10)	1.239(8)		
C–H		(1.095)	1.110(3)	1.108(2)	1.119(4)	1.114(2)
∠BBC		122[g]	121.8(8)	122.6(5)	120.0(13)	
∠BBH$_t$	119.9(9)	(120)	118.5(27)	(117.0)		
∠H$_b$BH$_b$	97.0(3)	96.6(3)[h]	97.6(7)	97.1(6)	95.2(35)	
∠BCH		(109.5)	112.5(26)	113.3(21)	112.0(20)	111.9(2)
B·C		2.943	2.955	2.964	2.973	
X[j]		1.729	1.733	1.750	1.715	
Y[j]		1.348	1.344	1.330	1.377	

[a] Distances in ångstroms, angles in degrees. MMDB a microwave determination, the others by electron diffraction with distances as r_a's for the DMDBs and r_g's for DB, TeMDB, and TMB; the uncertainties (in parentheses) are variously defined. [b] DB, MMDB, DMDB, TeMDB, and TMB: diborane(6); mono-, di-, and tetramethyldiborane(6); trimethylborane. [c] Reference 3a; see also Lafferty et al. (ref 3b) for an IR determination and Kuchitsu (ref 3c) for a joint consideration of the IR and ED results. [d] Reference 4b. [e] Reference 5a. [f] Reference 5b, ∠CBC$_{av}$ = 119.4 (3): [g] "Center-of-mass-fit parameter"; no uncertainty stated. [h] Calculated from H$_b$·H$_b$ = 1.99 (2) (ref 3b) and B–B = 1.773 (5). [i] Calculated from 1.840 (10) and 1.364 (45). [j] $X = r(\text{B–B})/2 + r(\text{B–C}) \cos \angle\text{BBC}$. $Y = r(\text{B–C}) \sin \angle\text{BBC}$.

trans isomers might be thought to represent a deficiency in the trans model, perhaps in not having a finite value for V_6. In our judgment, which of course involves detailed consideration of the radial distribution and intensity curves much more than just the R values, the difference is rather one of general data quality and method of drawing the backgrounds. The cis pictures were made more than a year later than the trans, after many small changes in equipment and procedure.

Discussion

This study has provided an unambiguous determination of which of the 1,2-DMDB's is cis and which is trans while finding the two molecules to be dimensionally almost identical in other respects. It has also helped to bring out the picture of the changes in bond length and bond angle that occur on substituting methyl for hydrogen in the diboranes and to throw some light on the interaction between the adjacent methyls in *cis*-DMDB and on the reason for its instability relative to the trans isomer. This picture is neither clear nor complete, as will be seen.

Bond Lengths and Bond Angles. The electron-diffraction structures of diborane and TeMDB invite comparison with the present results, trimethylborane and the microwave results on MMDB (Table III), as well as with the absent *gem*-DMDB and trimethyldiborane (TMB). The distances B–B, B–H$_b$, and B–H$_t$ generally increase with increasing substitution of CH$_3$ for H, except perhaps for MMDB. Ferguson and Cornwell's comment that the bridge bond in diborane derivatives "appears to be relatively insensitive to substitution at a terminal position", though rather strictly true for monobromodiborane, MMDB, and monochlorodiborane,[4] hardly applies to further substitution. Thus, TeMDB can no longer be regarded as exceptional merely because of its cis methyl–methyl repulsions:[4b] the increases in B–B, B–H$_t$, and B–H$_b$ are considerable, and substantially equal in the two DMDBs, but the B–B increase is little more than one-third of what it is in TeMDB; further, the increase in B–H$_b$ is about the same as in TeMDB. In the combinations X and Y of Table III, which are similar to ones used by Bartell in comparing TMB, TeMDB, and DB with some hydrocarbons,[5a] *cis*-DMDB and TeMDB stand out, suggesting a significant cis methyl–methyl repulsion that is overridden by *gem*-methyl–methyl repulsion in TeMDB. The BBC angles give the same impression. The B···C distances, on the other hand, vary with remarkable smoothness from MMDB to TeMDB.

Methyl Torsions. For *trans*-DMDB it was sufficient to assume an ethane-like three-fold barrier to methyl torsion, favoring the staggered conformation with respect to B–H$_t$ and (approximately) to B–H$_b$. The 2 kcal/mol found for the barrier height is consistent with the 2.61 kcal height deduced from the Raman spectrum of the solid.[14] It is also consistent with the 3 kcal of ethane[15-17] (which has shorter relevant bond lengths and full rather than approximate three-fold local symmetry), the 2 kcal of propene[18] and *trans*-2-butene[18,19] (each of which deviates greatly from this symmetry), and many others, but not with the 4.3 kcal reported for MMDB.[4b]

For *cis*-DMDB, in contrast, it seemed necessary, and is reasonable in view of the likely H···H repulsions between methyl groups, to add the sixfold component of eq 2. The resulting $V(\phi)$, with $V_3 = 1.5$ kcal/mol and $V_6 = -0.5$ kcal/mol, has minima $V \approx -30$ cal/mol·methyl, and is generally consistent with structural expectation, the barrier heights of related molecules, and the relative stabilities of *cis*- and *trans*-DMDB as compared to other cis–trans pairs. Modest repulsions are to be expected: the minimum H···H distance in the final cis model is 2.26 Å for $\phi_a = \phi_b = 0°$, 2.32 Å for $\phi_a = -\phi_b = \pm 15°$, and 2.38 Å for $\phi_a = \phi_b = \pm 15°$, the first two appreciably less than the conventional van der Waals distance, 2.4 Å. If so, the conformations of minimum total V have ϕ_a and ϕ_b equal at very roughly ±15° (each methyl rotated in the same direction as viewed down its own C–B bond) and the average H···H repulsion contributes to the apparent 0.8° widening of ∠BBC in cis over trans, as well as the decrease of V_3 from 2.0 to 1.5 and V_6 from 0 to −0.5. Further, if one makes the likely assumption that the basic threefold potential $V_a(\phi_a) + V_b(\phi_b)$ is the total potential for trans and is the same for cis as for trans, the contribution of this potential to the cis → trans isomerization energy is from classical statistics simply $2(\overline{V}_a^{(\text{trans})} - \overline{V}_a^{(\text{cis})}) = -0.4$ kcal/mol (see Appendix I) with

$$\overline{V}_a^{(\text{trans})} = \int_0^{2\pi} V_a(\phi) \exp(-V_a(\phi)/kT)\, d\phi \Big/ \int_0^{2\pi} \exp(-V_a(\phi)/kT)\, d\phi \quad (3)$$

$$\overline{V}_a^{(\text{cis})} = \int_0^{2\pi} V_a(\phi) \exp(-v_{\text{cis}}(\phi)/kT)\, d\phi \Big/ \int_0^{2\pi} \exp(-v_{\text{cis}}(\phi)/kT)\, d\phi \quad (4)$$

This would be the total isomerization energy if the methyl–methyl interaction potential consisted solely of hard-sphere repulsions, which affect the distribution in ϕ but contribute nothing directly to the energy. The actual repulsions are softer, so as to increase the cis energy, while the longer range attractions of the methyls will decrease it by a few tenths of a kilocalorie. For $V_3 = 0.7$ and $V_6 = 0$ (the best fit to the cis ED pattern if V_6 is constrained to zero), the basic $2(\overline{V}_d{}^{(\mathrm{trans})} - \overline{V}_a{}^{(\mathrm{cis})})$ (above) becomes −0.7 kcal/mol. The indication is that the isomerization energy is small and negative, or, if it is actually small and positive, that V_6 is more negative than our value. One contribution of methyl–methyl interaction in the cis entropy is surely positive (the single-methyl rotational barrier is lowered), but the inevitable restriction of methyl–methyl relative motion and possible increases in vibrational bending frequencies might overcome this and the calculated 0.2 cal K^{-1} mol^{-1} overall rotational difference. Taken altogether our bits of structural information about the presumed basic barrier and the methyl–methyl interaction do not seem inconsistent with the observed cis → trans equilibrium constant, which is about 1.2 at 293 K, with very small temperature dependence.[2]

cis-2-Butene also has a diminished barrier (0.75 kcal/mol[18-20]), but the conformational effect of the $CH_3 \cdots CH_3$ interaction (which surely is stronger in *cis*-2-butene than in *cis*-DMDB) is still unclear. The recent ED report on the 2-butenes[20] gives indications that the methyls are both distorted and dysrotated but makes no explicit determination of the barriers, while Kondo et al.[20] conclude from their very detailed microwave study, which included several deuterated species, that the stable conformation of the molecule belongs to point group C_{2v}.

Tetramethyldiborane also involves the cis barrier problem, but the reported threefold barrier of 1.0 kcal/mol[5a] is no doubt affected by geminal as well as vicinal methyl–methyl interaction. For the analogous tetramethylethylene the torsional conformation has perhaps still to be resolved: two ED studies[22] report twists of about 35°, but another[23] (the most recent) finds that no twist is needed.

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Supplementary Material Available. Tables of the experimental intensity data and the final backgrounds (13 pages). Ordering information is given on any current masthead page.

Appendix

Define a two-methyl torsional potential function, associated probability densities, and the one-methyl effective potential $v(\phi,T)$ by

$$V \equiv V(\phi_a,\phi_b) = V_a(\phi_a) + V_b(\phi_b) + V_{ab}(\phi_a,\phi_b) \equiv V_a + V_b + V_{ab}$$

$$P_{ab} \equiv P_{ab}(\phi_a,\phi_h) = \exp(-V/kT)/\iint \exp(-V/kT)\,\mathrm{d}\phi_a\,\mathrm{d}\phi_b$$

$$P_a \equiv P_a(\phi_a) = \int P_{ab}\,\mathrm{d}\phi_b \equiv \exp(-v(\phi_{a,T})kT)/\int \exp(v(\phi_{a,T})kT)\,\mathrm{d}\phi_a$$

with $0 \leqslant \phi_a,\phi_b \leqslant 2\pi$, and form the average

$$\overline{V} = \int V_aP_a\,\mathrm{d}\phi_a + \int V_bP_b\,\mathrm{d}\phi_b + \int V_{ab}P_{ab}\,\mathrm{d}\phi_a\,\mathrm{d}\phi_b \equiv \overline{V}_a + \overline{V}_b + \overline{V}_{ab}$$

If the groups are equivalent at equal angles $\phi_a = \phi_b$, then $V_a(\phi_a) = V_b(\phi_b)$ and $\overline{V} = 2\overline{V}_a + \overline{V}_{ab}$ follow. Writing *c* for cis and *t* for trans, assume $V_t = V_a + V_b$ and $V_c = V_a + V_b + V_{ab}$. This leads immediately to

$$V_t = 2V_a{}^{(t)} = 2\int V_aP_{a,t}\,\mathrm{d}\phi_a = 2\int V_a \exp(-v_t/kT)\,\mathrm{d}\phi_a/\int \exp(-v_t/kT)\,\mathrm{d}\phi_a$$

and

$$\overline{V}_c = 2\overline{V}_a{}^{(c)} + \overline{V}_{ab}{}^{(c)}$$

with

$$\overline{V}_a{}^{(c)} = \int V_a \exp(-v_c/kT)\,\mathrm{d}\phi_a/\int \exp(-v_c/kT)\,\mathrm{d}\phi_a$$

In eq 3 $v_t = V_a$ is written V_a. Note carefully that for cis the term V_{ab} both changes the densities (making v_c different from v_t) and contributes $V_{ab}{}^{(c)}$ to the total V_c.

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