Conformational Analysis. 9. 2,3-Dichloro-1,3-butadiene. An Electron-Diffraction Investigation of the Molecular Structure, Composition, and Anti–Gauche Energy and Entropy Differences

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Abstract: The structure of 2,3-dichloro-1,3-butadiene has been investigated by electron diffraction from the gas at nozzle temperatures of 293, 395, and 593 K. In addition to the expected more stable anti conformer ($\phi_A = 180°$), a less stable gauche conformer ($\phi_G \approx 52°$) was identified in mole fractions (with estimated 2σ uncertainties) of 0.028 (67), 0.073 (63), and 0.161 (58) at the low, intermediate, and high temperatures. These quantities correspond to $\Delta E° = E_G° - E_A° = 2.2$ ($2\sigma = 1.1$) kcal mol^{-1} and $\Delta S° + R \ln 2 = S_G° - S_A° + R \ln 2 = 0.35$ ($2\sigma = 2.2$) cal mol^{-1} K^{-1}. No temperature dependence of the distances and angles was seen, but the vibrational amplitudes were found to increase significantly as the temperature was increased. The values, with estimated 2σ uncertainties, of the principal distances (r_a) and angles ($\angle_\alpha$) for a "best" model comprising averages of the results from the three temperatures are $r(C-H) = 1.103$ (5) Å, $r(C=C) = 1.337$ (2) Å, $r(C-C) = 1.472$ (4) Å, $r(C-Cl) = 1.745$ (2) Å, $\angle C-C=C = 126.1$ (3)°, $\angle C-C-Cl = 115.2$ (3)°, $\angle C=C-H = 118.7$ (15)°, and $\angle \phi_G = 52.3$ (97)°. These results include allowance for the effects of vibrational averaging (shrinkage). The usual assumption that the parameter values of the two forms are indistinguishably different except for the torsion angle was adopted.

A part of the program of structure study in this laboratory has dealt with simple conjugated molecules such as the substituted butadienes and the oxalyl halides. One aspect of major interest is the conformation of the gaseous molecules. Butadiene itself has been found to be planar anti.[1] The substituted butadienes have been found to be either planar anti[2–6] or nonplanar gauche,[7–10] at least at normal temperatures. In the oxalyl halides,[11,12] however, a less stable gauche form coexists with the anti in substantial amounts (~30–40%) at temperatures near 0 °C.

So far as the butadienes are concerned, the molecules with gauche conformations are those in which large steric interactions between atoms substituted at the 1 and 3 or 2 and 4 positions would operate were the molecules to be planar anti. The molecule 2,3-dichloro-1,3-butadiene (hereafter DCB) is expected to have a rather modest 1,3-type interaction, and indeed the IR spectra of the solid,[13,14] liquid,[13] and gas,[14] the Raman spectrum of the liquid,[14] the NMR spectra in solution,[14] and the electron-diffraction data,[15] all at room temperature or below, have been interpreted[13–16] as arising from the planar anti conformer. There is, however, an interesting question: does a second conformer exist together with the anti form in DCB but in amounts too small at low temperatures to have been detected by the methods mentioned? An argument to this effect may be made as follows. The isoelectronic molecules biacetyl (2,3-butanedione) and 2,3-dimethylbutadiene have similar bond configurations and are observed only in the planar anti form,[6,17,18] even, in the case of the former, at sample temperatures up to 520 °C.[18] Since DCB and oxalyl chloride are also isoelectronic and have similar bond configurations, one might expect DCB to exist in both anti and gauche conformations (Figure 1) as does oxalyl chloride. That such is the case is suggested by electric field deflection experiments[19] in which sample polarity was observed at 0 °C and found to increase with increasing temperature. We report here electron-diffraction results for DCB at three sample temperatures. These results include identification of a higher energy gauche conformation in the presence of a lower energy anti form. Although data from the previous experiment[15] at room temperature were available, it was thought best to repeat that experiment under conditions as nearly like those of the planned higher temperature experiments as possible.

Experimental Section

Samples of DCB were obtained from E. I. du Pont de Nemours in the form of a 50% solution in *o*-dichlorobenzene containing a small amount

of phenothiazine as an inhibitor. DCB was distilled from the solution under reduced pressure (100 torr) with use of a 40-cm column packed with glass helices. The product was stored in liquid N_2 until immediately before use.

Diffraction photographs were made in the Oregon State apparatus at nozzle temperatures of 293, 395, and 593 K. Experimental conditions were as follows: sector shape, r^3; plates, 8 × 10 in. Kodak projector slide, medium contrast; development, 10 min in D-19 diluted 1:1; ambient apparatus pressure, 4.0 × 10^{-6} to 1.0 × 10^{-5} torr; exposure times, 45–150 s; beam currents, 0.35–0.50 µA; nominal nozzle-to-plate distances, 745 mm (long) and 300 mm (middle); nominal electron wavelength, 0.058 Å (calibrated in separate experiments with CO_2: $r_a(C=O) = 1.1646$ Å and $r_a(O \cdot O) = 2.3244$ Å).

Three plates from each of the two camera distances at each temperature were selected for analysis. The ranges of intensity data were 2.50 $\leqslant s \leqslant 12.00$ (Å^{-1}) (long camera) and 7.50 $\leqslant s \leqslant 29.50$ (Å^{-1}) (middle camera); the data interval was $\Delta s = 0.25$ Å^{-1}. Procedures for obtaining the total intensities ($s^4 I_t(s)$) and the molecular intensities ($s I_m(s)$) have been described.[20,21] Figure 2 shows the $s^4 I_t(s)$ curves and the calculated

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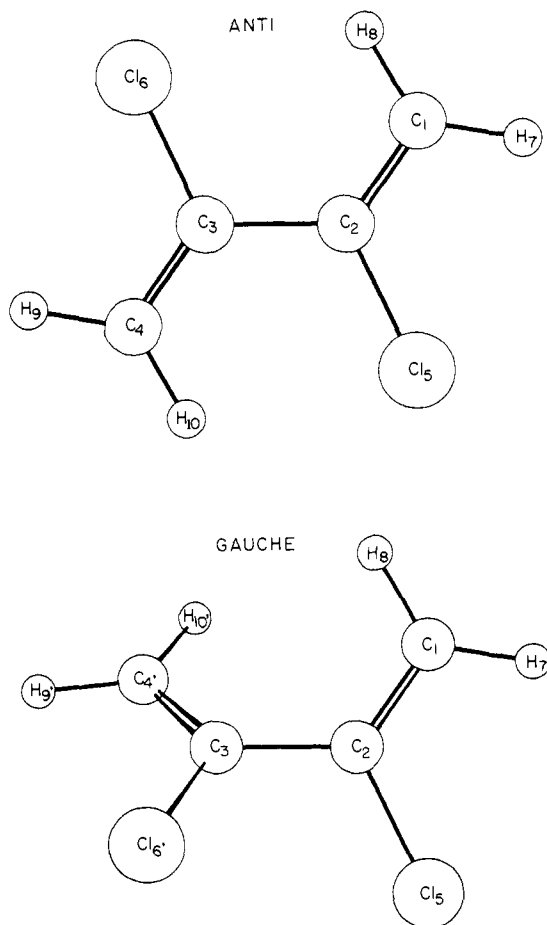[†] On leave from the University of Trondheim, Trondheim, Norway.

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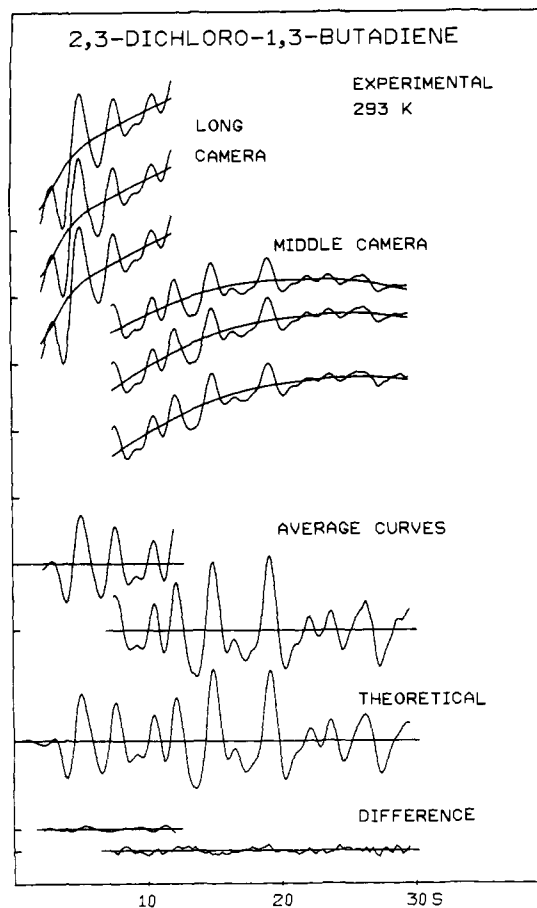**Figure 1.** Atom numbering for the conformers of 2,3-dichloro-1,3-butadiene.

Figure 2. Intensity curves. Curves $(s^4 I_t)$ from each plate magnified 5× are shown superimposed on their backgrounds. Average curves are $s(s^4 I_t$ − bkgd). The theoretical curve corresponds to the 293 K model of Tables I and II.

backgrounds for the 293 K experiment. Similar figures for the other temperatures as well as all the intensity and background data are available as supplementary material.

The radial distribution curves (Figure 3) were calculated in the usual way by Fourier transformation of functions $I_m'(s) = Z_C Z_{Cl} A_C^{-1} A_{Cl}^{-1} s I_m(s)$. Amplitudes and phases for all calculations were obtained from tables.[22]

Structure Analysis

The presence of more than one conformer in the gaseous sample of DCB is seen in the temperature dependence of the peak at 4.3 Å in the radial distribution curves. The peak, which corresponds to the Cl··Cl distance in the anti form, decreases in area with increasing temperature at the same time as area in the region expected for the Cl··Cl distance in a gauche form, 3.0–3.3 Å, appears to increase.

In nearly all our studies of conformational equilibria, it has been possible to construct a satisfactory model of the system with the assumption that the conformers have the same structure except for the torsion angles. This, together with the assumption that the C=CH$_2$ groups have local C_{2v} symmetry, leads to ten parameters for specification of the DCB system. Convenient parameters were r_α(C—H), r_α(C=C), r_α(C—C), r_α(C—Cl), $\angle_\alpha$Cl—C=C, $\angle_\alpha$C—C—Cl, $\angle_\alpha$C=C—H, the rms amplitude of the torsional vibration of the anti form, σ_A, the torsion angle for the gauche form, $\angle\phi_G$, and the mole fraction of the gauche form, X_G. Conversion of the structurally consistent set of r_α distances to r_g and to r_a for use in the scattered intensity formula was done in a fashion very similar to that recently described for propenoyl chloride.[23] The C_{2h} symmetrized quadratic force field used to
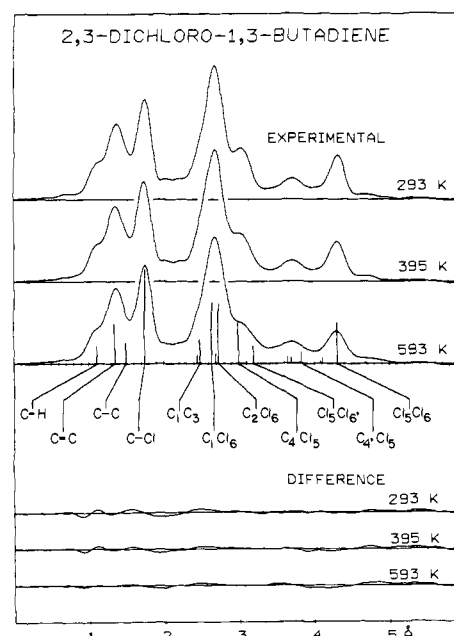
Figure 3. Radial distribution curves. The lengths of the vertical bars are proprotional to the weights of distances. Bars for nonbond distances involving hydrogen are unlabeled.

calculate the distance–conversion terms for the anti form reproduced the observed wavenumbers[12] to within 1 cm^{-1}. Since a

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Table I. Results for Structural Parameters of 2,3-Dichlorobutadiene[a]

parameter	293 K	395 K	593 K	best model[b]	ref 15
r(C—H)	1.101 (11)	1.105 (9)	1.103 (8)	1.103 (5)	1.100 (10)
r(C=C)	1.341 (4)	1.335 (3)	1.338 (3)	1.337 (2)	1.346 (3)
r(C—C)	1.463 (8)	1.474 (5)	1.474 (6)	1.472 (4)	1.465 (5)
r(C—Cl)	1.744 (3)	1.744 (2)	1.748 (2)	1.745 (2)	1.747 (2)
∠C—C=C	126.0 (4)	126.2 (3)	126.1 (3)	126.1 (2)	126.9 (2)
∠C—C—Cl	115.8 (5)	115.1 (4)	115.5 (5)	115.2 (3)	114.7 (3)
∠C=C—H	120.6 (25)	120.3 (28)	120.2 (25)	118.7 (15)	[120.0]
∠ϕ_G[c]	[52.3]	[52.3]	52.3 (97)	52.3 (97)	
σ_A[d]	6.0 (63)	8.4 (50)	11.0 (48)		[0]
X[e]	0.972 (67)	0.927 (63)	0.839 (58)		
R[f]	0.083	0.071	0.055		

[a]Distances (r_a) in angstroms, angles ($\angle_a$) in degrees. Values in parentheses are estimated 2σ. [b]Weighted average of results from three temperatures. [c]Torsion angle for gauche form $\angle\phi_A = 180°$. [d]Root mean square torsional amplitude for anti form. [e]Mole fraction of anti form. [f]$R = |\sum w_i\Delta_i^2/\sum w_i(s_iI_i(\text{obsd}))^2|^{1/2}$ where $\Delta_i = s_iI_i(\text{obsd}) - s_iI_i(\text{calcd})$.

Table II. Distances (r) and Amplitudes (l) in 2,3-Dichlorobutadiene[a,b]

	293 K				395 K				593 K				best model	293 K (ref 15)	
	r_a[c]	l_{exptl}[d]	l_{calcd}	$D/10^{-3}$	r_a[c]	l_{exptl}[d]	l_{calcd}	$D/10^{-3}$	r_a[c]	l[d]	l_{calcd}	$D/10^{-3}$		r_a[c]	l[d,e]
C—H	1.101 (11)	0.052 (10)	0.077	21	1.105 (9)	0.053 (9)	0.077	23	1.103 (8)	0.069 (7)	0.077	29	1.108 (18)	1.100 (10)	[0.070]
C=C	1.341 (4)	0.052}(8)	0.043	7	1.335 (3)	0.043}(6)	0.044	8	1.338 (3)	0.048}(4)	0.045	11	1.340 (4)	1.346 (3)	0.039 (4)
C—C	1.463 (8)	0.057}	0.048	2	1.474 (6)	0.048}	0.049	3	1.474 (6)	0.054}	0.051	4	1.475 (9)	1.465 (5)	[0.048]
C—Cl	1.744 (3)	0.050 (4)	0.048	8	1.744 (3)	0.053 (3)	0.051	11	1.748 (2)	0.058 (3)	0.056	15	1.745 (3)	1.747 (2)	0.039 (3)
$C_2\cdot H_7$	2.116 (24)	0.075 (25)	0.102	19	2.108 (27)	0.101 (27)	0.103	23	2.106 (24)	0.108 (22)	0.107	31	2.105 (64)	2.122 (9)	[0.100]
$C_1\cdot C_3$	2.498 (10)	0.052 (9)	0.059	4	2.502 (8)	0.054 (7)	0.062	5	2.501 (8)	0.075 (8)	0.070	7	2.505 (11)	2.515 (7)	[0.065]
$C_1\cdot Cl_5$	2.653 (7)	0.058}(5)	0.063	10	2.656 (7)	0.067}(5)	0.069	13	2.655 (8)	0.078}(5)	0.079	20	2.662 (10)	2.666 (4)	0.055}
$C_2\cdot Cl_6$	2.719 (6)	0.055}	0.061	5	2.716 (6)	0.064}	0.066	7	2.724 (7)	0.074}	0.076	10	2.716 (7)	2.708 (4)	0.055}(3)
$C_3\cdots H_8$	2.766 (42)		0.140	13	2.764 (48)		0.146	16	2.763 (42)		0.160	22	2.741 (78)	2.784 (9)	[0.120]
$Cl_5\cdots H_7$	2.780 (40)		0.147	14	2.780 (45)		0.155	18	2.772 (38)		0.173	25	2.760 (72)	2.791 (7)	[0.120]
$C_3\cdots H_7$	3.474 (18)		0.099	9	3.479 (19)		0.100	11	3.475 (17)		0.105	15	3.471 (32)	3.495 (12)	[0.120]
$Cl_5\cdots H_8$	3.676 (14)		0.098	19	3.629 (14)		0.101	24	3.677 (12)		0.108	34	3.676 (25)	3.694 (11)	[0.140]

Anti

	293 K				395 K				593 K				best model	293 K (ref 15)	
$Cl_5\cdots H_{10}$	2.622 (52)		0.175	24	2.601 (58)		0.189	30	2.609 (53)		0.217	44	2.597 (95)	2.618 (7)	[0.120]
$C_4\cdots Cl_5$	3.043 (8)	0.090 (9)	0.092	9	3.032 (9)	0.104 (9)	0.104	11	3.039 (10)	0.132 (15)	0.124	18	3.042 (18)	3.045 (6)	0.078 (5)
$C_1\cdots C_4$	3.726 (12)	0.072 (29)	0.064	2	3.722 (11)	0.085 (30)	0.067	2	3.719 (10)	0.097 (30)	0.075	3	3.728 (14)	3.758 (9)	[0.075]
$C_1\cdots H_{10}$	4.092 (42)		0.141	6	4.082 (46)		0.147	8	4.076 (41)		0.161	10	4.065 (76)	4.127 (11)	[0.120]
$Cl_5\cdots H_9$	4.128 (14)		0.118	11	4.120 (13)		0.128	13	4.124 (14)		0.146	19	4.129 (22)	4.144 (12)	[0.120]
$Cl_5\cdots Cl_6$	4.317 (7)	0.067 (6)	0.061	1	4.306 (8)	0.080 (5)	0.067	2	4.312 (9)	0.099 (7)	0.079	2	4.306 (9)	4.316 (5)	0.060 (4)
$C_1\cdots H_9$	4.602 (25)		0.111	6	4.597 (26)		0.114	7	4.591 (24)		0.122	9	4.589 (44)	4.638 (13)	[0.120]

Gauche

	293 K				395 K				593 K				best model		
$C_1\cdots H_{10'}$	3.096 (49)		0.194	23	3.099 (54)		0.211	30	3.104 (112)		0.245	44	2.96 (12)		
$C_1\cdots C_{4'}$	3.190 (17)		0.100	12	3.197 (13)		0.111	16	3.200 (50)		0.132	24	3.14 (6)		
$Cl_5\cdots Cl_6'$	3.280 (17)		0.131	6	3.254 (17)		0.151	8	3.273 (105)		0.183	12	3.14 (12)		
$C_4\cdots Cl_5$	3.836 (6)		0.081	2	3.826 (6)		0.090	3	3.830 (58)		0.107	4	3.90 (5)		
$C_1\cdots H_{9'}$	4.225 (21)		0.121	16	4.233 (17)		0.130	20	4.232 (38)		0.147	29	4.20 (4)		
$Cl_5\cdots H_{10'}$	4.165 (41)		0.164	6	4.153 (46)		0.177	7	4.151 (106)		0.202	10	4.26 (16)		
$Cl_5\cdots H_{9'}$	4.687 (23)		0.124	6	4.623 (27)		0.131	10	4.676 (46)		0.146	10	4.72 (8)		

[a]In angstroms. [b]Quantities in parentheses are estimated 2σ. [c]$r_a = r_\alpha + \delta r + K - l^2/r = r_\alpha + D - l^2/r = r_g - l^2/r$. [d]Quantities in braces were refined as a group. Unspecified amplitudes were assigned the calculated values. [e]Quantities in brackets were assumed.

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Table III. Correlation Matrix for Parameters of 2,3-Dichlorobutadiene at 593 K (×100)

		$\sigma_{LS}{}^a$ ×100	r_1	r_2	r_3	r_4	$\angle 5$	$\angle 6$	$\angle 7$	σ_8	$\angle 9$	l_{10}	l_{11}	l_{12}	l_{13}	l_{14}	l_{15}	l_{16}	l_{17}	l_{18}	X_A
1	$r(C—H)$	0.28	100	26	29	-21	2	-12	-31	-5	-14	14	-45	-14	4	1	1	-2	5	7	-11
2	$r(C=C)$	0.09		100	46	-10	18	-32	-37	-16	-12	40	-24	-26	21	7	24	-15	2	5	-9
3	$r(C—C)$	0.19			100	-29	13	-52	-42	-17	-10	20	-30	-11	18	8	26	-28	3	5	0
4	$r(C—Cl)$	0.05				100	35	-11	12	8	5	-7	28	-2	-13	5	8	2	0	-4	2
5	$\angle C—C=C$	10.1					100	-36	27	-31	-2	5	-8	-25	12	-22	-13	32	5	17	-25
6	$\angle C—C—Cl$	17.1						100	38	55	-6	-12	7	7	-9	6	-66	1	8	4	-19
7	$\angle C—C—H$	88.1							100	20	-4	-13	16	14	1	-29	-46	21	12	5	0
8	$\angle\sigma_A{}^b$	170								100	2	-6	7	7	-7	16	-27	-18	8	-11	-3
9	$\angle\phi_G$	350									100	-3	0	-4	0	-8	0	54	-46	7	-21
10	$l(C—H)$	0.28										100	-29	-8	12	4	10	-5	2	1	-2
11	$l(C=C)$	0.09											100	27	-12	8	15	-7	-3	-2	16
12	$l(C—Cl)$	0.05												100	-12	15	26	-17	2	1	27
13	$l(C_2\cdot H_7)$	0.84													100	-12	-7	8	0	3	-7
14	$l(C_1\cdot C_3)$	0.26														100	39	31	1	6	13
15	$l(C_1\cdot Cl_5)$	0.25															100	-27	-6	-13	40
16	$l(C_4\cdot\cdot Cl_5)$	0.35																100	-22	21	-48
17	$l(C_1\cdot\cdot C_4)$	0.33																	100	4	-9
18	$l(Cl_5\cdot\cdot Cl_6)$	0.27																		100	-49
19	X_A	2.07																			100

^{a} Standard deviations from least squares. Distances (r) and amplitudes (l) in angstroms; angles in degrees. ^{b} Rootmean square torsional amplitude.

vibrational spectrum for the higher energy conformer has not been observed, the same force constants, resymmetrized to C_2, were used for it. There are a large number of vibrational amplitude parameters. Some were assigned values calculated from the force field, and some were gathered into groups wherein amplitude differences of group members were taken from the calculations. The symmetry coordinates, force constants, and wavenumbers are found in the supplementary material.

Refinements of the system were carried out by least-squares fitting of a theoretical intensity distribution to the two average intensities for each temperature. For investigation of the parameter σ_A, we followed the method described previously[11] whereby pseudoconformers with structures defined by $\Delta\phi = 180 - \phi_A{}^{24} = 0, \pm\sigma_A/2, \pm\sigma_A, \pm 3\sigma_A/2$, and $\pm 2\sigma_A$ were introduced with weights $P(\phi) = Q^{-1}\exp[-(\Delta\phi)^2/2\sigma_A{}^2]$. The perpendicular amplitude corrections for the torsion-sensitive distances in the pseudoconformers were calculated with elimination of the effects of the torsional mode.

It was found that because of uncertainties connected with measurements of small amounts of the gauche form at the lower two temperatures, the parameter $\angle\phi_G$ could not be reliably determined at these temperatures and it was given the value 52.3° obtained from the high temperature refinements. Toward the end of the work the validity of our assumption that the structures of the two forms of DCB are the same except for the torsion angle was partially explored by allowing for a possible difference in the lengths of the C–Cl bonds. Test refinements indicated this distance difference to be unsignificantly different from zero.

The final results obtained for the structure of DCB at each of the three temperatures are given in Tables I and II; the three similar correlation matrices are represented by that for the highest temperature result given in Table III. Although one might have expected the bond distances to increase a few thousandths of an angstrom from the lowest to the highest temperature due to vibrational anharmonicty, no such effect is seen in them nor in the nonbond distances and bond angles. It is, thus, appropriate to propose, so far as geometry is concerned, a "best model" comprising the weighted average of the three sets of results. The parameter values of this model are also found in Tables I and II. Those describing the anti form of the molecule are presumably more precise than those for the gauche form, since the torsion angle for the latter was measured only at the highest temperature.

Discussion

Tables I and II also contain results from our early work[15] on 2,3-dichlorobutadiene in which no allowance was made for the effects of vibrational averaging (shrinkage). Since these effects amount to some hundredths of an angstrom in some cases, the agreement of the values for the structural parameters with the present ones must be regarded as very satisfactory. Some of the amplitude values differ appreciably from the present 293 K values, but the amplitude assumptions in the two investigations were so different that the comparison has little meaning.

Comparison of the values found for various types of distances and bond angles in chlorine-substituted 1,3-butadienes reveals only small differences. Comparison of those for DCB with their correlates in 1,3-butadiene itself shows the conjugated single bond to be a bit longer (1.472 (4) Å vs. 1.467 (1) Å[1c] or 1.463 (3) Å[1b]) and the C=C—C angle to be a bit larger (126.1 (5)° vs. 122.8 (5)° [1c] or 123.3 (5)° [1b]). Each of these may reflect greater steric repulsion between methylene hydrogens and the chlorines in DCB than between the correspondingly located hydrogens in 1,3-butadiene.

The relationship of DCB to 1,3-butadiene is similar to that of oxalyl chloride to glyoxal. Since the two conformers of isoelectronic butadiene and glyoxal are anti and (likely) syn,[25] and those of oxalyl chloride[11] anti and gauche, it is not surprising that the conformers of DCB, isoelectronic with oxalyl chloride, are also anti and gauche. Nor is it surprising that the equilibrium, which is shifted in favor of the anti form to a greater extent in butadiene than in glyoxal, also favors this form in DCB to a greater extent than in oxalyl chloride. These observations are consistent with greater conjugation stabilization for both the anti and syn forms in the C=C—C=C groups than in the O=C—C=O, combined with the steric repulsion between atoms bound to C_2 and C_3 that operates most strongly in the syn conformation. Thus, the gauche torsion angle for DCB is about the same as in oxalyl chloride (52 (10)° vs. 55 (6)°), and the Cl··Cl distance is in each case about 3.2 Å. (The Cl··Cl van der Waals distance is about 3.6 Å).

The quantities $\Delta E° = E_G° - E_A°$ and $\Delta S° = S_G° - S_A°$ may be determined from the usual formula $R \ln (N_G/N_A) - R \ln 2 = -\Delta E°/T + \Delta S°$, where the statistical weight of the gauche form

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(24) In previous papers of this series we adopted $\phi_A = 0$ as the reference torsion angle.

(25) By "syn" we intend "synperpiplanar", or a conformation within ±30° of planar. For butadiene, see, for example: Bock, C. W.; George, P.; Trachtman, M.; Zanger, M. *J. Chem. Soc., Perkin Trans. 2* **1979**, *2*, 26. For glyoxal see: Durig, J. R.; Tong, C. C.; Li, Y. S. *J. Chem. Phys.* **1972**, *57*, 4425.
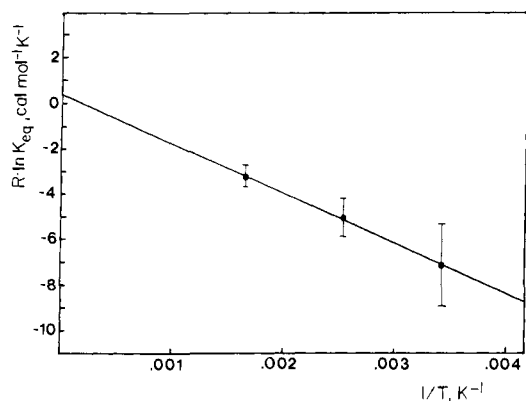
Figure 4. van't Hoff plot. $K = N_G/N_A$.

has been removed from $S_G{}^\circ$. The van't Hoff plot shown in Figure 4 yields the results $\Delta E^\circ = 2.2$ ($2\sigma = 1.1$) kcal mol^{-1} and $\Delta S^\circ + R \ln 2 = +0.35$ ($2\sigma = 2.2$) cal mol^{-1} K^{-1}.

To the extent that torsion around the conjugated single bond is a good representation of one of the normal coordinates in DCB, our parameter σ_A provides a crude estimate of the wavenumber for the torsional mode.[11] The result, calculated from the formula $\omega = (2\pi c)^{-1}(k/\mu_I)^{1/2}$ with $k = 0.24$ ($2\sigma = 0.06$) aJ rad^{-2} ($k = V^*/2 = RT/\sigma_A{}^2$; the value is a weighted average), is 87 ($2\sigma = 11$) cm^{-1}, in excellent agreement with the observed 80 cm^{-1}.

Supplementary Material Available: Tables of total intensities, final background, and average molecular intensities for three temperatures, symmetry coordinates, force constants, and observed wavenumbers, and figures of total intensities with backgrounds for 395 and 593 K experiments (24 pages). Ordering information is given on any current masthead page.
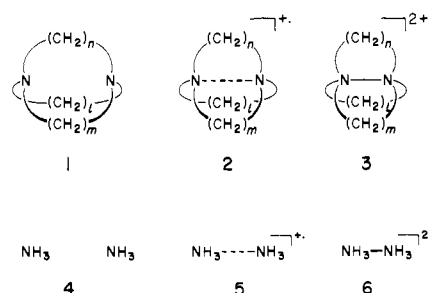
Hydrazinium Radical Cation (NH₃NH₃⁺·) and Dication (NH₃NH₃²⁺): Prototypes for the Ionized Forms of Medium-Ring Bicyclic Compounds

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Abstract: Ab initio molecular orbital theory has been used to study the hydrazinium radical cation (NH₃NH₃⁺·, **5**) and dication (NH₃NH₃²⁺, **6**) as prototypes for the ionized forms of medium-ring bicyclic compounds. The radical cation **5** is characterized by a long N···N bond (2.164 Å) but is nevertheless bound by 134 kJ mol⁻¹ with respect to NH₃ + NH₃⁺·. In the dication **6**, the N–N bond is markedly reduced (to 1.442 Å). Although dissociation of **6** to 2NH₃⁺· is exothermic by 249 kJ mol⁻¹, this process involves a large activation barrier (194 kJ mol⁻¹). The results suggest that suitably constructed propellane analogues of **6** involving appropriate-sized bridges might exhibit bond-stretch isomerism.

The chemistry of medium-ring bicyclic compounds has flourished recently in the hands of Alder and co-workers.[1–5] In particular, they have been able to synthesize a variety of bicyclic diamines (**1**) and the corresponding radical cations (**2**) and dications (**3**). These systems are of theoretical interest since they

include constrained interbridgehead interactions involving four, three, and two electrons, respectively. The characterization of the resulting rather unusual bonds is a tempting target for theoretical investigation. The medium-ring bicyclic systems themselves (**1–3**) are rather too large to lend themselves to reliable ab

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