Tetrahedron Letters, Vol.22, No.31, pp 2945 - 2948, 1981
Printed in Great Britain

0040-4039/81/312945-04$02.00/0

1,3-INTERACTIONS AMONG THREE POLAR BONDS. 2-CHLOROMETHYL-2-METHYL-1,3-DICHLOROPROPANE

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Abstract: The ^{1}H DNMR spectrum for the title compound at 102K complemented by molecular orbital and empirical force field calculations reveal the presence of three preferred equilibrium conformations with slightly different free energies.

1,3-Interactions are ubiquitous in small molecules and polymers. A recently published ^{1}H dynamic NMR (DNMR) study of 2,2-dimethyl-1,3-dibromopropane(**1**)[1] and a subsequent unpublished examination of 2,2-dimethyl-1,3-dichloropropane(**2**) in our laboratory revealed a strong preference for one molecular geometry (C_2 symmetry) in these simple systems. The results for **1** and **2** suggested that DNMR studies of mutual 1,3-interactions among three polar bonds in comparably simple molecules would also be successful and informative.

The ^{1}H DNMR spectrum (270 MHz) of 2-chloromethyl-2-methyl-1,3-dichloropropane (**3**; 5% v/v in $CBrF_3$) at 167K shows two singlets at δ3.54 (6H; CH_2Cl) and δ1.21 (3H; CH_3) as illustrated in Figure 1. At lower temperatures, the CH_2Cl resonance decoalesces and is sharpened into a relatively complex spectrum at 102K (Figure 1). A theoretical simulation of the spectrum at 102K is shown as the "composite" spectrum in Figure 2. The composite spectrum may be decomposed into three subspectra (i.e., three conformers) including a dominant species (58%) which gives a singlet (δ3.64) and an AB spectrum (δ3.69, δ3.16, ^{2}J = -10.4 Hz) as illustrated at the top of Figure 2. The area ratio of the singlet (see asterisk in Figure 2) to the AB spectrum is 1:2. The second most populous subspectrum (34%) consists of three AB spectra all of equal area (δ3.88, δ3.63, ^{2}J = -11.2 Hz; δ3.74, δ3.46, ^{2}J = -12.4 Hz; δ3.57, δ3.09, ^{2}J = -12.3 Hz) shown as the second spectrum from the top in Figure 2. The least populous subspectrum (8%) consists of a single AB spectrum (δ3.93, δ3.26, ^{2}J = -12.3 Hz) shown in Figure 2. The three separate subspectra at the top of Figure 2 were computed without the introduction of any exchange broadening. However, at 102K which is the lowest temperature at which meaningful spectra could be recorded, the CH_2Cl spectrum is subject to slight exchange-broadening. An accurate simulation of this spectrum is achieved by superposition of the top three spectra of Figure 2 and the introduction of a rate constant ($k \sim 15\ sec^{-1}$) for exchange among the two minor subspectra but no exchange involving the major subspectrum (see composite spectrum in Figure 2).

The spectrum of **3** at 102K reveals a richer mixture of conformers than for **1** and **2**. For **3**, it then becomes necessary to identify the NMR-detectable conformers. Both MINDO/3 semi-empirical molecular orbital calculations[2] and MM2 empirical force field calculations[3] indicate

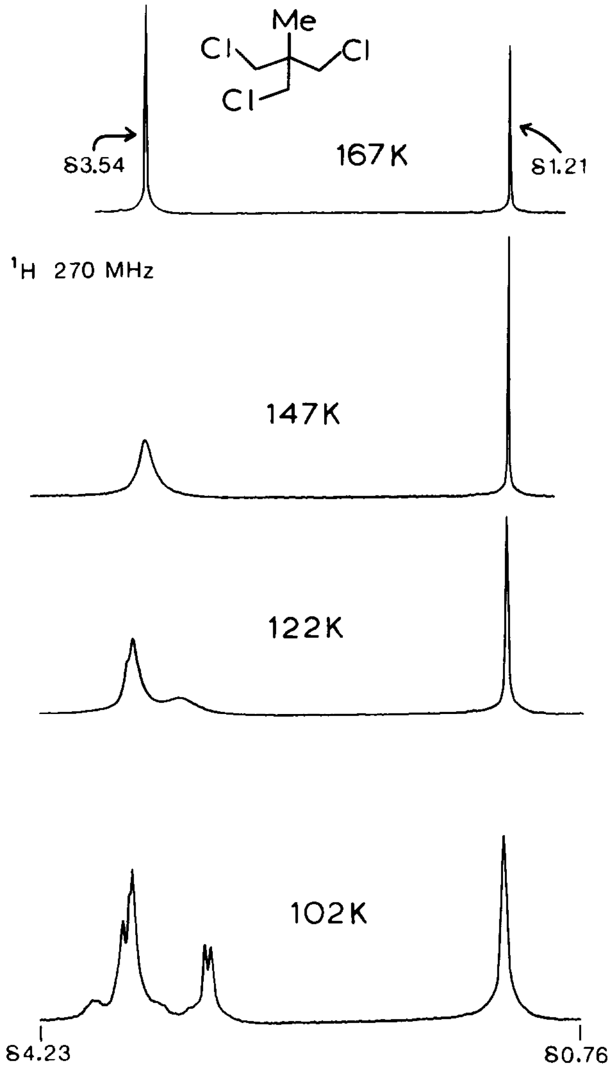


Figure 1

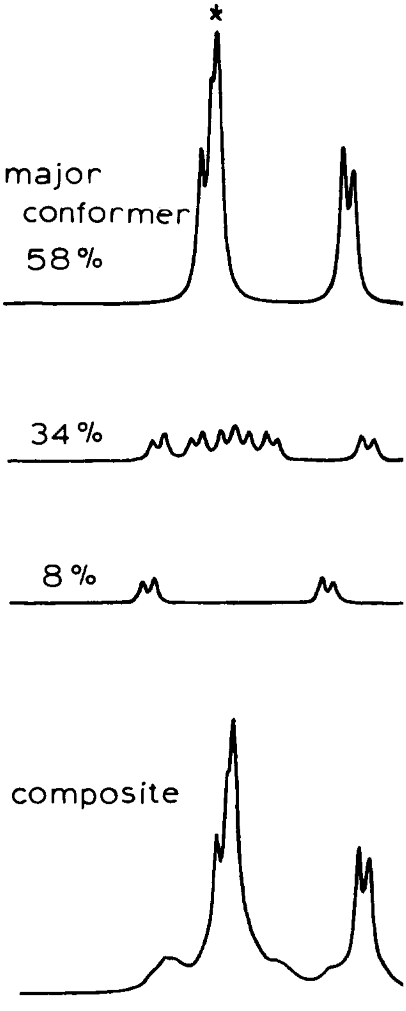
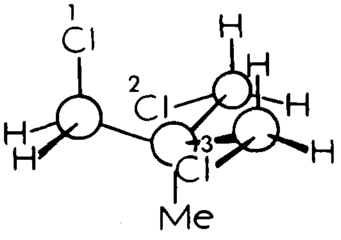


Figure 2



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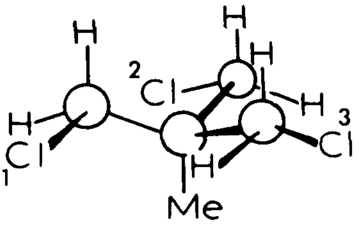

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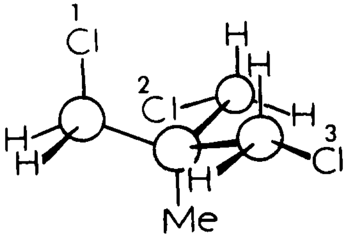

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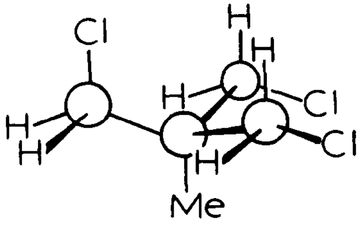

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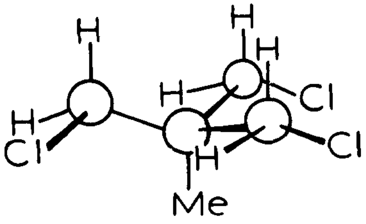

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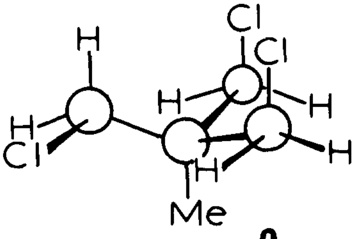

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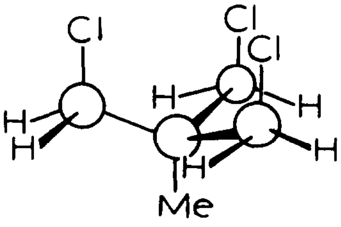

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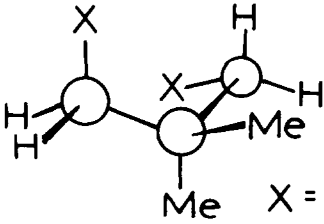

X = Cl, Br

11

that conformers **4**-**6** have comparable energies and, by the MM2 method, are at least 2 kcal/mole more stable than **7**-**9** and 6 kcal/mole more stable than **10**. These results are consistent with an essentially exclusive preference of cis-1,3-dichlorocyclohexane for the diequatorial conformer indicating a strong repulsive interaction between two chlorines which are syn and 1,3 to each other.[4] Indeed, the dipole moments of **4**(1.90D), **5**(1.90D), and **6**(1.94D) computed using the MM2 method[3] are significantly smaller than the 3.71D value calculated for **7**-**9** and the 5.66D value for **10**. Experimentally measured dipole moments of 1.79D[5] and 2.1D[6] for **3** are consistent with the dominance of conformers **4**-**6** but provide no information regarding the relative amounts of **4**-**6**.

The ^1H DNMR spectrum of **3** at 102K is consistent with a preference for rotamers **4**-**6**. The major CH_2Cl subspectrum (Figure 2) is perfectly consistent with the symmetry of **4**, i.e., a singlet and two superimposed AB spectra. The subspectrum composed of three different AB spectra is then assigned logically to **6**. The subspectrum composed of just one AB spectrum is assigned to **5** in which there are indeed only two types of methylene protons. From a decomposition of the spectrum at 102K, free energy differences may be calculated: $\Delta G^\circ\ (\mathbf{6} \rightleftarrows \mathbf{4}) = -0.1$ kcal/mole; $\Delta G^\circ\ (\mathbf{5} \rightleftarrows \mathbf{4}) = -0.4$ kcal/mole.

The spatial relationship between the chlorines numbered 1 and 2 and between chlorines numbered 1 and 3 in conformer **4** is identical to that between the two halogens in the strongly preferred (exclusive by NMR) C_2 rotamers of **1** and **2** (see **11**).[1] In **6**, only one such pair-wise relationship exists between the chlorines numbered 1 and 2, and there are no such orientations of any two chlorines relative to one another in **5**. In light of the fact that the preference for **11** in the dihalides is essentially exclusive, the preference for conformer **4** in the trichloride is not surprising. However, whatever factors lead to the exclusive preference for **11** in the dihalides, they are not sufficient to cause an exclusive preference for **4** in the trichloroneopentane. Indeed, rotamers **5** and **6** account for 42% of the total of all conformer populations.

The results reported here are consistent with an electron-diffraction study of **3** at 361K which revealed the presence of **4**,**5** and **6**[7], and also consistent with an IR study of **3** which indicated that **4** is the dominant conformation.[5]

Acknowledgement: We are grateful to the National Science Foundation for support (grant no. CHE79-26243 and CHE79-16210).

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(Received in USA 22 January 1981)