3.3 2-Trichloromethyl-1,3,2-thioxapholpholane-2-oxid. The white crystal was recrystallized from acetone and chloroform to give fine crystal of 2-trichloromethyl-1,3,2-thioxaphospholane-2-oxide, the yield was 5.9 g (47%). m.p 117–119°.

Elem. anal. Obs. (calc. %): Cl, 44.2(44.1), H, 1.6(1.6). IR: 2920 m., 1360 m, 1255 vs, 1220, 1180 m, 1010 vs, 950 s, 770 s, 680 w. NMR: δ 4.5 (mul. O-CH_2, 2H), δ 3.67 (tri. S-CH_2), 2H). Mass spect.: *m/e* (rel. intens. %): 242.3 (M , 3.2), 123.2 (100), 97.2(10.0), 59.2(15.4), 47.1(19.9).

3.4 2-Trichloromethyl-1,3,2-oxazaphospholane-2-oxide. To 14.1 m*l* (0.1 mole) of triethylamine dissolved in 50 m*l* of drying ethylether was added 3.1 m*l* (0.05 moles) of 2-aminoethanol. The flask is flushed with nitrogen and placed on a magnetic stirrer, and the reaction flask was placed in a dry ice-ice bath, and added dropwise 12.2 g (0.05 moles) of trichlolomethylphosphonyl dichloride and 40 m*l* of ethylether.

The resulting solution was stirred for 18 hours at 15°, and the mixture was filtered through a glass filter.

The filtrate was concentrated on rotatory evaporator, and the remaining solid was dissolved in water, and unsoluble solid was collected on a glass filter, washed with 10 m*l* of water, and dried in a desiccator. The yield was 4.2 g(41%). m.p 131–133°.

Elementary Analysis: Obs. (calc. %) C, 16.3(16.04), H, 2.3(2.22), N, 6.2 (6.23). IR (KBr) : 3250 cm^{-1} (N-H), (s) 2990, 1910 (m), 1470, 1405 (m), 1290, 1255 (s) 1080, 1005 (vs), 940 (m), 880, 780 (m). NMR ($CDCl_3$) δ 4.5 (O-CH_2, mult.), δ 4.1 (N-H, broad), δ 3.6 (mult., N-CH_2). (DMSO): 6.4, 6.8 (broad, N-H), δ 4.5 (O-CH_2, mult.), δ 3.5 (N-CH_2, mult.). Mass spestra: *m/e* (rel. intens. %) 187.9 (0.5), 106.1(100) 47.0(24.9), 79.1 (15.1).

4. Monoesterification of trichloromethylphosphonyldichloride

4.1 O-Ethyl trichloromethylchlorophosphonate

$C_3H_5Cl_4O_2P$: b.p 92 (6 mmHg)

IR (NaCl plate):

2980 cm^{-1} (m), 1290 cm^{-1} (s), 1020 cm^{-1} (vs), 870 cm , 760 cm (s)

NMR (CCl_4):

4.5 (2H, mul.), 1.5 (3H, trip.)

4.2 O-2-Chloroethyltrichloromethylchlorophosphonate.

$C_3H_4Cl_5O_2P$: b.p 131 (4mmHg)

IR (NaCl plate): 2980 cm^{-1} (m), 1290 cm^{-1} (s), 1075 cm^{-1} (s), 1020 cm^{-1} (vs), 970 cm^{-1} (m), 870, 780, 760 cm^{-1} (m)

NMR ($CDCl_3$):

δ 3.7 (2H, trip.), 4.6 (2H, mutl.)

4.3 O-2,2,2-trichloroethylthrichloromethylchloropholphonate

$C_3H_2Cl_6O_2P$: m.p 102–103°

IR(KBr):

3000, 1445, 1290 cm^{-1} (s), 1090, 1020 cm^{-1} (vs), 850, 770 cm^{-1}

NMR($CDCl_3$): δ 4.8 (mul.)

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MO Studies of Configurations and Conformations (IX). Molecular Structure of Sulfamoyl Chlorides

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Semi-empirical MO calculations were performed to investigate stereochemical properties of sulfamoyl chlorides; R_2NSO_2Cl Where R=H or CH_3 It was found that for all the molecules considered the most preferred conformation was the form in which $n_N-\sigma^*_{SCl}$ conjugative interaction is a maximum and the least favored conformation was the form in which steric repulsion is large due to eclipsing of Cl and R. In case of the molecule with no symmetry *i.e.*, CH_2NHSO_2Cl, the stability was also dependent upon nonbonded interactions between the eclipsing groups.

Introduction

Recently a number of structural studies employing electron diffraction have been reported on molecules with S-N bond. General structural features found are: (a) there is at least one synmetry plane, (b) the two bonds and the lone pair of the nitrogen stagger the sulfur bonds and lone pairs.

Within the Hartree-Fock self-consistent field (SCF) framework, energy change, ΔE_T, associated with the internal rotation can be decomposed into two separate contributions: (a) one-electron factor, $\Delta(2\sum\epsilon_i)$, which includes "through-space"[2] and "through-bond"[3,4] interactions, and (b) steric factor, $\Delta(V_{nn}-V_{ee})$, where v_{nn} and v_{ee} represent the internuclear and interelectronic repulsions respectively.

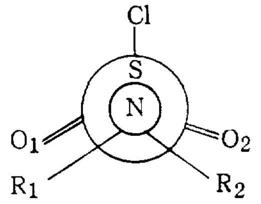
$$\Delta E_T=\Delta(2\sum^{occ}\epsilon_i)+\Delta(V_{nn}-V_{ee}) \qquad (1)$$

It is now apparent that in many cases the one-electron factor is more important in determining stereochemical preferences of molecules than the steric factor owing to the near cancellation of ΔV_{nn} and ΔV_{ee}[4]. Thus it is found that a qualitatively useful stereochemical determination is possible even with such a crude approximation as the extended Hückel theory (EHT) which employs only the orbital energies $(2\sum\epsilon_i)$ to calculate the total energy, E_T, and various semi-empirical methods are widely employed to investigate conformational properties of large molecules.[5]

As a part of our MO theoretical structural studies we have performed semi-empirical calculations on sulfamoyl chlorides, R_2NSO_2Cl, where R=H or CH_3. In this work, we strived to show MO theoretical origins of conformational preferences sulfamoyl chlorides.

Calculations

The EHT (without 3-d orbitals), EHT-SPD (with 3d-orbitals) and CNDO/2 (with 3-d orbitals) programs used in the calculation were those obtained from the QCPE, and bond lengths and angles adopted were the experimental values.[1a] We have kept the molecular geometry fixed except for the torsional angle θ of internal rotation around the S-N bond.[1a] The torsional angle θ was varied from the eclipsed form (I) rotating SO_2Cl around the S-N axis by 60, 90, 120, 180, 240 and 300° clockwise, and each component of the total energy expression (1) together with charges and overlap populations were examined.

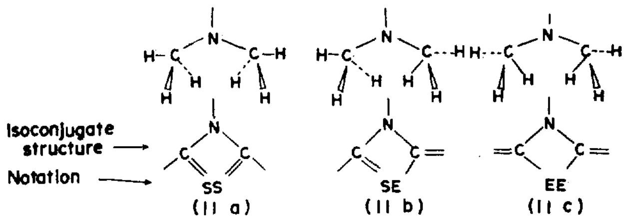


(I)

$\theta=0°$

$R_1=R_2=H,\ CH_3$

For molecules with a symmetry plane at $\theta=0$, *i.e.*, for $R_1=R_2=H$ and $R_1=R_2=CH_3$, $\theta=240$ and 300° need not be considered. The following three formes were considered for conformations of methyl groups in N,N-dimethylsulfamoyl chloride.



Results and Discussion

Sulfamoyl Chloride: H_2NSO_2Cl. Three methods of calculation were employed for this molecule; EHT, EHT-SPD and CNDO/2. Results of calculation are summarized in Table 1. Relative energies and overlap populations of S-N and S-Cl bonds are presented graphically in Figure 1. Structural features common to all three method of calculation are: (1) the most stable form is the rotamer with $\theta=180°$ which agrees with the result of electron diffraction studies

TABLE 1: Relative Energies (ΔE_T in kcal/mol), Overlap populations (P_{XY}) and Charges (Z_X) for Rotation (θ) Around S-N of NH_2SO_2Cl

Method of Calon	θ	ΔE_T	P_{SN}	P_{SCl}	P_{SO_1}	Z_S	Z_N	Z_{Cl}	Z_{O_1}
EHT	0	2.3	0.606	0.214	0.554	3.57	−0.96	−0.57	−1.43
	60	3.1	0.594	0.220	0.553	3.78	−0.98	−0.55	−1.43
	120	2.9	0.597	0.216	0.554	3.58	−0.97	−0.56	−1.43
	180	0.0	0.617	0.206	0.552	3.56	−0.91	−0.58	−1.43
EHT/SPD	0	2.2	1.059	0.914	1.263	1.81	−0.47	−0.15	−0.86
	60	1.9	1.055	0.923	1.239	1.81	−0.47	−0.14	−0.88
	120	2.7	1.054	0.917	1.261	1.81	−0.46	−0.15	−0.86
	180	0.0	1.068	0.904	1.272	1.78	−0.42	−0.17	−0.86
CNDO/2	0	5.5	0.899	0.785	1.209	0.43	−0.23	−0.01	−0.24
	60	6.0	0.863	0.785	1.205	0.43	−0.23	−0.01	−0.25
	120	6.3	0.913	0.783	1.207	0.43	−0.20	−0.03	−0.24
	180	0.0	0.922	0.733	1.210	0.41	−0.20	−0.03	−0.23

of Hargittai[1a] and the least stable form is that with $\theta=120°$; (2) the most stable form corresponds to the form with the largest overlap population for atom pair SN (P_{SN}) and the smallest overlap population for atom pair SCl (P_{SCl}); (3) the most stable form has the smallest positive charge on S atom and the smallest negative charge on N atom; (4) the most stable form has the largest negative charge on Cl atom; (5) when d-orbitals are included in the calculation, *i.e.*, with the EHT-SPD and CNDO/2, it is the most stable form that has the largest overlap population for atom pair SO (P_{SO_1}) and the smallest negative charge on atom O_1.

It is quite noteworthy that the EHT without 3-d orbitals also gives qualitatively correct predictions of the most and the least preferred forms.[6] However Table 1 shows that the EHT methods, especially the EHT without 3-d orbitals, give grossly exaggerated charges in contrast with the more realistic values of the CNDO/2 method.[3] The structural features (2)-(4) above are best accounted for by the dominating influence of vicinal bond-antibond interactions on the conformational stability;[3] conjugative interaction of the lone pair on the N atom with the σ^* orbital of S-Cl bond becomes maximum (and hence the stabilizing effect becomes maximum) when the two orbitals are arranged in the *trans* orientation as in the rotamer with $\theta=180$. As this type of σ conjugative interaction involves the charge transfer from a filled nonbonding orbital to a vacant antibonding orbital, $n_N \rightarrow \sigma^*_{SCl}$, consequences of this interaction will be exactly what we obtained as the structural features (2)-(4) above.[3b] Further support for this view may be provided by the energy component analysis, since the stabilizing effect of conjugative through-bond interactions should be reflected in the one-electron factor in equation (1). Variations of energy components calculated by the CNDO/2 method are given in Table 2.

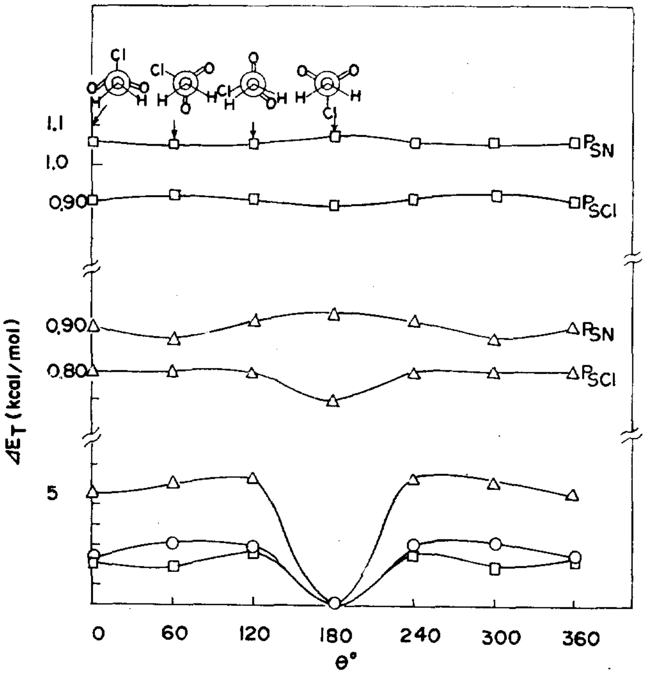


Figure 1. Relative energies, ΔE_T, and overlap populations, P_{XY}, as a function of torsional angle θ for NH_2SO_2Cl (○: EHT, □: EHT-SPD, △: CNDO/2).

It can be seen from this table that the most preferred form ($\theta=180°$) has the largest stabilizing one-electron factor ($\Delta(2\sum\epsilon_i)$) which more than compensates for the destabilizing effect of steric factors, $\Delta(V_{nn}-V_{ee})$, of equation (1); the conformational preference of the form with $\theta=180°$ is dominated by the stabilizing one-electron factor which includes the σ conjugative interactions. On the other hand,

TABLE 2: Energy Component Analysis for NH_2SO_2Cl by CNDO/2 Method (kcal/mol).

θ	ΔE_T	$\Delta 2\sum\epsilon_i$	ΔV_{nn}	$\Delta(V_{nn}-V_{ee})$
0	5.5	68.5	−32.6	−63.0
60	6.0	60.6	−29.7	−54.7
120	6.3	27.5	13.2	6.9
180	0.0	0.0	0.0	0.0

TABLE 3: Relative Energies (ΔE_T in kcal/mol) Overlap Populations (P_{XY}) and Charges (Z_X) for Rotation (θ) Around S-N of CH_2NHSO_2Cl.

Method of	θ	ΔE_T	P_{SN}	P_{SCl}	P_{SO_1}	Z_S	Z_N	Z_{Cl}	Z_{O_1}
EHT	0	3.7	0.619	0.208	0.552	3.55	−0.85	−0.57	−1.43
	60	3.8	0.606	0.217	0.552	3.55	−0.88	−0.56	−1.43
	120	7.9	0.605	0.215	0.551	3.54	−0.87	−0.56	−1.43
	180	0.0	0.632	0.197	0.550	3.52	−0.80	−0.59	−1.44
	240	3.9	0.609	0.209	0.554	3.55	−0.86	−0.57	−1.43
	300	3.7	0.601	0.218	0.552	3.57	−0.89	−0.55	−1.43
EHT-SPD	0	2.7	1.077	0.913	1.264	1.82	−0.46	−0.15	−0.87
	60	2.6	1.075	0.924	1.241	1.82	−0.46	−0.14	−0.88
	120	10.9	1.079	0.921	1.258	1.81	−0.45	−0.17	−0.86
	180	0.0	1.089	0.907	1.266	1.79	−0.41	−0.18	−0.86
	240	2.9	1.073	0.916	1.256	1.82	−0.45	−0.15	−0.87
	300	0.8	1.073	0.920	1.240	1.82	−0.46	−0.14	−0.86
CNDO/2	0	8.3	0.909	0.784	1.212	0.40	−0.18	−0.02	−0.23
	60	6.7	0.905	0.783	1.208	0.42	−0.17	−0.02	−0.24
	120	8.8	0.902	0.781	1.208	0.42	−0.17	−0.04	−0.23
	180	0.0	0.911	0.780	1.210	0.40	−0.15	−0.04	−0.23
	240	4.5	0.902	0.781	1.207	0.42	−0.17	−0.04	−0.25
	300	6.6	0.905	0.783	1.204	0.42	−0.18	−0.02	−0.25

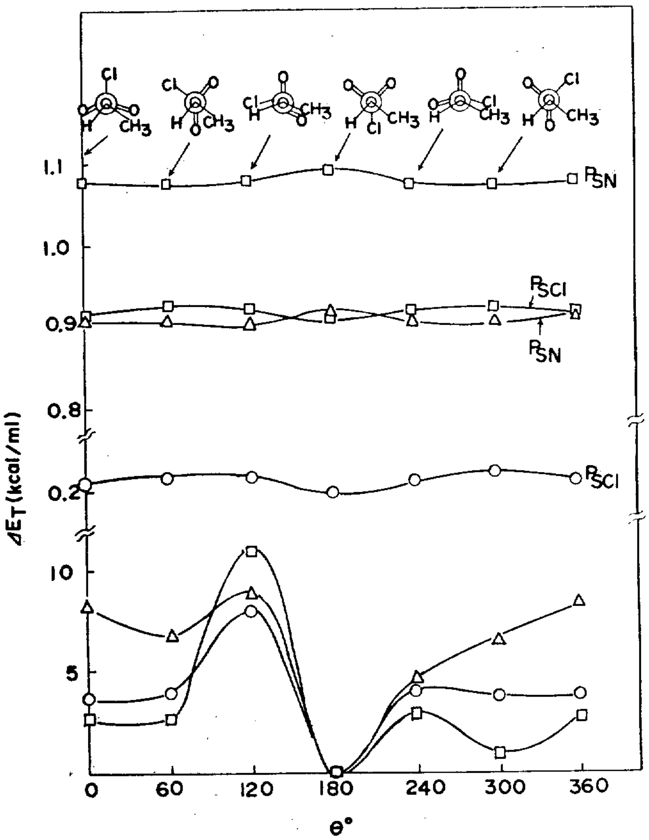
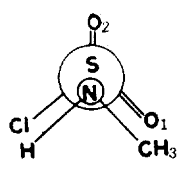


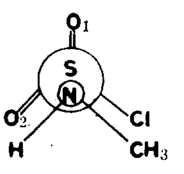
Figure 2. Relative energies, ΔE_T, and overlap populations, P_{XY}, as a function of torsional angle θ for CH_3NHSO_2Cl (o:EHT, □:EHT-SPD, △:CNDO/2).

the origin of instability of the form with $\theta=120°$ is the dominant destabilizing steric effect. The barrier of rotation (rigid) around S-N bond is the difference in total energy, ΔE_T, between these two extremes; it ranges from 3 (by EHT method) to 6 (by CNDO/2) kcal/mol.

N-Methylsulfamoyl Chloride; CH_3NHSO_2Cl, ($R_1=H$, $R_2=CH_3$ in I). In this molecule R_1 and R_2 are different, and therefore conformations with $\theta=60°$ and 120° will be different from those with $\theta=300°$ and 240° respectively. Results of calculations are shown in Table 3, and presented partly in Figure 2. Structural features common to all the three method of calculation for this molecule are the same as listed (1)-(5) above for NH_2SO_2Cl. The most preferred form is again that with $\theta=180°$ which has the lone pair of the N atom arranged trans relative to the S-Cl bond; the stabilizing effect of through-bond, n-σ^*, interaction is maxinum in this form as indicated by the overlap populations and charges. The least favored form is that with $\theta=120°$, (III), in which the Cl eclipses the H on N atom.



$\theta=120°$
(III)



$\theta=240°$
(IV)

TABLE 4: Energy Component Analyses for CH_3NHSO_2Cl by CNDO/2 (kcal/mol)

θ	ΔE_T	$\Delta 2\Sigma\epsilon_i$	ΔV_{nn}	$\Delta(V_{nn}-V_{ee})$
0	8.3	75.7	−220.1	−67.4
60	6.7	75.7	−328.1	−69.1
120	8.8	40.8	−174.3	−32.0
180	0.0	0.0	0.0	0.0
240	4.5	3.0	+327.3	−1.4
300	6.7	54.7	−29.7	−48.1

TABLE 5; Relative Energies for Various Conformations of Methyl Groups on N for $(CH_3)_2NSO_2Cl$ by EHT-SPD Method (kcal/mol)

Relative energy		Angle of S-N rotation (θ)				
		0°	60	90	120	180
ΔE_T	SS	0.0	0.0	0.0	0.0	0.0
	SE	5.2	3.8	7.3	5.0	3.8
	EE	14.6	11.7	11.7	24.4	24.5

Energy component analysis in Table 4 shows that the form with $\theta=240°$, (IV), has the largest steric repulsion owing to the eclipsing of two bulky groups, Cl and CH_3, but the approach of Cl to CH_3 also increases nonbonded, through-space,[2] interaction, which is reflected in the reatively large stabilizing one-electron effect for this conformation as compared with the form (III). The energy difference of 4.3 kcal/mol between these two forms (ΔE_T (E_{III}-E_{IV}) 4.3 kcal/mol) is seen to be dominated by one-electron factor; the form (III) has less favorable one-electron effect although it is more favored sterically over the form (IV). These analyses again confirm the importance of one-electron factor in determining stereochemical preferences although it is the balance of two factors, one-electron and steric, that determine conformational preferences.[2b] Table 3 shows that the (rigid) rotational barrier for this molecule ranges from 8 to 11 kcal/mol. according to the three methods of calculation.

N,N-Dimethylsulfamoyl Chloride: $(CH_3)_2NSO_2Cl$. Two methyl groups on the nitrogen were found to favor SS conformation; in general the order of stability is SS>SE>EE as shown in Table 5. According to the FMO interpretation of nonbonded interactions,[7] this order can be explained in terms of π-isoconjugate structure; the SS conformation has a ($6\pi/5$) system, and the SE and EE have ($5\pi/4$) and ($4\pi/3$) systems respectively. It has been shown that 6 electron crowded system is a 4N+2 system which is the most stabilizing (end-to-end attractive), while 4π electron crowded system is a 4N system which is the most destabilizing (end-to-end repulsive).

Energetics and eigenvector properties calculated with fixed methyl conformations to SS are summarized in Table 6, and partly presented in Figure 3.

In general structural features common to both methods of calculation are the same as listed (1)-(5) above for NH_2SO_2Cl with minor exceptions in the case of CNDO/2 calculations; the stability of the form with $\theta=180°$ is again dominated by the through-bond, n-σ^*, interaction. Eclipsing of two bulky groups, Cl and CH_3, in the form with $\theta=120°$ again

TABLE 6: Relative Energies (ΔE_T in kcal/mol), Overlap Populations (P_{XY}) and Charges (Z_X) for Rotation (θ) Around S-N of $(CH_3)_2$ NSO_2Cl

Method of calcn	θ	ΔE_T	P_{SN}	P_{SCl}	P_{SO_1}	Z_S	Z_N	Z_{Cl}	Z_{O_1}
EHT-CPD	0	3.0	1.093	0.913	1.261	1.83	−0.46	−0.16	−0.87
	60	1.4	1.091	0.921	1.266	1.83	−0.45	−0.15	−0.87
	90	7.9	1.092	0.925	1.258	1.83	−0.46	−0.16	−0.88
	120	11.1	1.096	0.920	1.259	1.82	−0.45	−0.17	−0.87
	180	0.0	1.107	0.909	1.267	1.79	−0.40	−0.19	−0.87
CNDO/2	0	11.6	1.253	1.152	1.373	0.41	−0.13	−0.03	−0.25
	60	12.1	1.243	1.151	1.373	0.41	−0.13	−0.03	−0.24
	120	16.5	1.238	1.153	1.378	0.37	−0.15	−0.04	−0.22
	180	0.0	1.260	1.151	1.374	0.39	−0.11	−0.05	−0.23

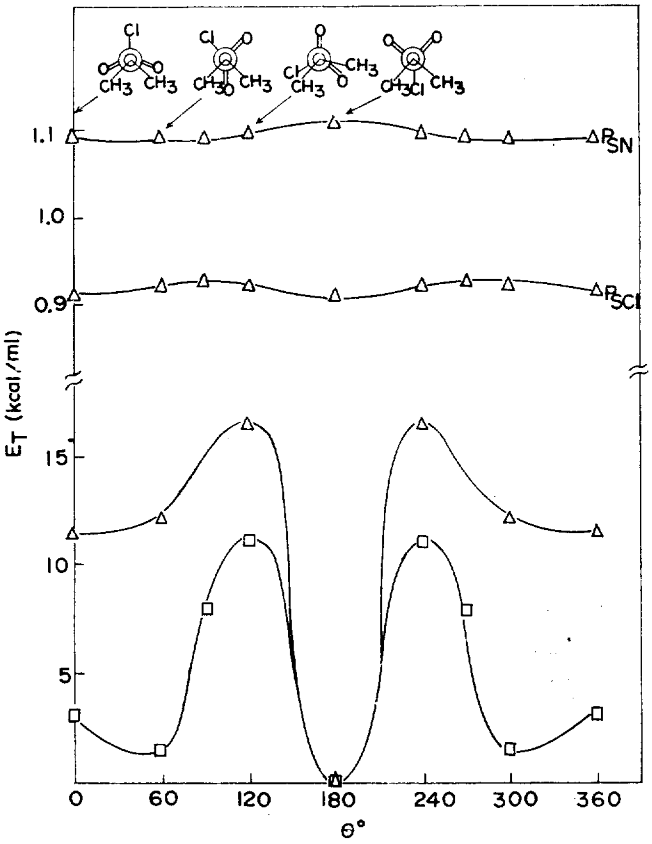
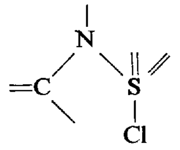


Figure 3. Relatine energies, ΔE_T, and Overlap Populations, P_{XY} as a function of tarrional angle θ for $(CH_3)_2$ NSO_2Cl (□: EHT-SPD, △: CNDO/2).

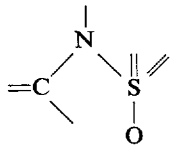
TABLE 7: Energy Component Analysis for $(CH_3)_2NSO_2Cl$ by CNDO/2 (kcal/mol)

θ	ΔE_T	$\Delta(2\sum\epsilon_i)$	ΔV_{nn}	$\Delta(V_{nn}-V_{ee})$
0	11.6	109.3	−407.4	−97.2
60	12.1	83.7	−328.1	−71.1
120	16.5	−38.8	171.7	55.8
180	0.0	0.0	0.0	0.0

causes large steric repulsion, which has the dominant influence in the structural instability of the form. Another interesting feature of this form ($\theta=120°$) can be found in Table 7; the form ($\theta=120°$) has more stabilizing one-electron effect, $\Delta(2\sum\epsilon_i)$, as compared with the most stable form ($\theta=180°$). Analyses of π-isoconjugate structures give two π-systems of possible one-to-end attraction; structure (V) in the form with $\theta=120°$ is a ($6\pi/4$) and (VI) in the form with $\theta=180°$ is a ($5\pi/4$) system, which are both nonbonded attractive systems.[7] The structure (V) was also found in the



(V)



(VI)

form with $\theta=240°$ of CH_3 $NHSO_2$ Cl above, which was the main reason why this form had more stability inspite of large steric repulsion as compared to the form with $\theta=120°$. The barrier height for rotation around S-N bond in $(CH_3)_2$ NSO_2Cl is again higher with the CNDO/2 method; 16.5 kcal/mol with the CNDO/2 and 11.1 kcal/mol with the EHT-SPD method.

We therefore conclude that: for all the molecules considered in this work, the most preferred conformation is the form with $\theta=180°$ in which n-σ^* conjugative interaction is a maximum, and the least favored conformation is the form with $\theta=120°$ in which steric repulsion is large due to eclipsing of Cl and R. In case of the molecule with no symmetry plane *i.e.*, CH_3NHSO_2Cl the instability of the form with $\theta=120°$ is dominated by the unfavorable nonbonded interactions between the eclipsing groups.

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The Charge Transfer Complexes of Monoalkylbenzene with Iodine in Carbon Tetrachloride (I)

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Ultraviolet spectrophotometric investigations have been carried out the systems of monoalkylbenzene with iodine in carbon tetrachloride. The results reveal the formation of one to one molecular complexes. The equilibrium constants for these complexes of representative monosubstituted benzene reveal the following order of increasing stability: benzene <methyl- <ethyl- <*n*-propyl-benzene. The value of ΔH, ΔG, and ΔS for interaction of a number of monoalkyl substituted benzene with iodine has been determinated. In general, as ΔH becomes increasingly negative, corresponding decreases in ΔG and ΔS values are observed, and these variation are linear. The thermodynamic constants become increasingly negative with increasing monoalkyl substitution of the aromatic donor nucleus. The complex bond is therefore weak, and its formation is accompanied by relatively small entropy changes.

Introduction

Benesi and Hildebrand[1] observed that a solution of benzene and iodine in carbon tetrachloride had a maximum of absorption at 297 *mu*. They concluded that this was due to the formation of a one-to-one molecular complex, benzene-iodine, in the solution. In a similar study, Keefer and Andrews[2] found a different absorption maximum for the benzene-iodine complex, namely 292 $m\mu$. In the same publication, the authors report on the interaction of iodine monochloride with ehtyl-, isopropyl-, and *t*-butylbenzenes. On the whole, it can be said that the agreement between the results the two groups of authors have obtained is not too satisfactory.

Carrying out ultraviolet spectrophotometric studies to measure the temperature dependence of complex formation, Keefer and Andrews[3] determined ΔH, ΔG and ΔS for carbon tetrachloride solutions of iodine with polyalkylbenzenes. For iodine compolexes with benzene and toluene and related electron donors[4~7], heats of formation lying between -1 and -2 kcal/mole have been obtained.

In these previous studies, however, equilibrium constants and thermodynamic functions of monoalkylbenzene-iodine complexes have not been investigated so far. It therefore appeared to be interest to extend the studies to monoalkylbenzene-iodine systems in carbon tetrachloride, in order to determine the relative complexing power of iodine with monoalkylbenzenes. In the present study, spectrophotometric investigations are reported carried out to determine the temperature dependence of one-to-one complex formation in the cases of iodine and a series of monoalkylated benzenes of rather differing donor strengths in carbon tetrachloride.

Experimental

Materials. Samples of Merck Co. iodine (superpure grade) and benzene, toluene, carbon tetrachloride (uvasol grade) were used without further purification. Samples of Merck Co. ethylbenzene, *n*-propylbenzene (synthese grade) were dried over calcium chloride and distilled through a 100 cm distillation column packed with glass helices. The reflux ratio was kept at approximately 1:15. The middle portions of the distillates were collected. The boiling points and refraction index observed were as follows: ethylbenzene; b.p 136.3°, n^{20} *D* 1.4960, *n*-propylbenzene; b.p 159.0°, n^{20} *D* 1.4922.

Preparation of Stock Solutions. The solution of iodine in carbon tetrachloride was prepared by weighting an appropriate quantity of iodine into a volumetric flask, and a adding carbon tetrachloride solvent to make up to volume. The solution thus prepared was diluted further to suitable concentrations. The solutions of monoalkylbenzenes (donors) in carbon tetrachloride was prepared by weighting an appropriate quantity of donors into a volumetric flask and adding carbon tetrachloride to make up to volume. Each solution was freshly prepared at room temperature, 24±1°C, before making absorption spectrum measurements and wrapped with black paper to prevent any photochemical reaction in solution. The concentration of iodine was *ca.* 10 mole·l^{-1} and that of donors was 10 mole·l^{-1}. These were varied at least three fold for any one system. Both concentrations were adjusted so as to keep the absorbancy within suitable limits.