A Conformational Study on Some Thiobenzophenones. Molecular Orbital Calculations

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(Received December 27, 1986)

MO calculations were performed on the different conformers of thiobenzophenone and on the planar conformer of a number of its derivatives using the INDO-CI procedures. A nonplanar conformer with an angle of 15° between the planes of benzene rings was predicted for thiobenzophenone. Dipole moment and charge density were calculated and correlated to the reactivity of the studied molecules. A Gaussian analysis was performed on the spectra of the studied compounds, results compared satisfactorily with the results of MO calculations.

Relatively, little work has been done on the MO calculations of thiobenzophenone especially in the recent years. However, many spectral studies have been reported on thiones, thiourea and many of their derivatives.

The effect of substitution,1) solvent,2) and irradiation3) on the electronic spectra of thiobenzophenone have been reported. The spectrum of a crystal of thiobenzophenone—doped in a crystal of benzophenone—at 20K indicated that the transition along the C=S direction is intrinsically allowed.4) Simple molecular orbital calculations (HMO) were performed on some aliphatic and aromatic thiocarbonyl compounds,5–8) a linear correlation was observed between the wave number of the $n \rightarrow \pi^*$ transition and the Hückel excitation energy.

The crystal structure of thiobenzophenone and thiobenzophenone *S*-oxide were determined, the former is monoclinic whereas the latter is orthorhombic.9) The photoelectron helium (HeI) spectra of aromatic thiocarbonyls and the corresponding *S*-oxides were determined. For thioketones the ordering of the outermost MO's is: n(S), π_7, π_6, π_5, π_4, π_3, n(S) being the HOMO.

Electron-rich olefins react with n,π^* triplet state of thiobenzophenone yielding 1,4-dithiane or thietane depending on the structure of the olefins whereas electron deficient olefins react with π,π^* singlet states of thiobenzophenone.11) Photocycloaddition of thiobenzophenone to olefins substituted with electron releasing groups lead to the formation of 1,4-dithianes.12) However, if the electron-rich olefins are substituted with bulky substituents their photocycloaddition to thiobenzophenone result in thietane and not dithiane derivatives.13) Photocycloaddition of thiobenzophenone to olefins substituted by electron-withdrawing groups result in the formation of thietane derivatives through a nucleophilic attack on the olefin.14) It was shown that the π,π^* state plays a role in the reaction which proceeds only on irradiation by 366 nm light.

In this work, INDO-CI molecular orbital calculations were performed on different conformers of thiobenzophenone and the planar conformers of a number of its derivatives. Gausian analysis of the spectra was performed. These results have not been reported before.

Method of Calculations

The all valence-electrons INDO method of calculations was followed. Details and parameterization are found elsewhere.15) Interaction was considered between nine electronic configurations in which electrons are transferred from the three highest occupied MO's to the three lowest unoccupied MO's. If the wave function of an electronic configuration is ψ_m, the CI wave function ψ_{CI} is given by $\sum_m a_m \psi_m$. The energies of the resulted states are calculated by solving the determinant

$$\det\{H_{mn} - E\delta_{mn}\} = 0. \qquad (1)$$

The diagonal elements are the expectation values of the energies of the different configurations whereas the off-diagonal elements of H_{mn} are the expectation values of the Hamiltonian averaged between the two configurations *m* and *n*. Calculation of the diagonal and off-diagonal elements of Eq. 1 requires the calculations of the integrals:

$$\varepsilon_{ij} = <\psi_i|H_{\text{core}}|\psi_j>$$
$$\gamma_{ii} = (\psi_i\psi_i|\psi_i\psi_i)$$
$$\gamma_{ij} = (\psi_i\psi_i|\psi_j\psi_j)$$
$$\delta_{ij} = (\psi_i\psi_j|\psi_j\psi_i)$$
$$\zeta^{jl}_{ik} = (\psi_i\psi_k|\psi_j\psi_l)$$

Substituting the LCAO epression for the molecular orbitals (ψ) one gets16)

$$\varepsilon_{ij} = \sum_{\mu\nu} C_{i\mu}C_{j\nu} <\phi_\mu|H_{\text{core}}|\phi_\nu>$$
$$\gamma_{ii} = \sum_{\mu\nu} C^2_{i\mu}C^2_{i\nu}\,(\mu\nu|\nu\nu)$$
$$\gamma_{ij} = \sum_{\mu\nu} C^2_{i\mu}C^2_{j\nu}\,(\mu\nu|\nu\nu)$$
$$\delta_{ij} = \sum_{\mu\nu} C_{i\mu}C_{j\nu}C_{i\nu}C_{j\nu}\,(\mu\mu|\nu\nu)$$
$$\zeta^{jl}_{ik} = \sum_{\mu\nu} C_{i\mu}C_{k\mu}C_{j\nu}C_{l\nu}\,(\mu\mu|\nu\nu)$$

The letters *i*, *j*, *k*, and *l* refer to MO's whereas μ,ν, to AO's. The diagonal and off-diagonal elements of Eq. 1 are calculated as follows[17)]

$$<\psi_G|\hat{H}|\psi_G>=2\sum_{i=1}^{n}\varepsilon_i+\sum_{i}^{n}\sum_{i}^{n}(2\gamma_{ij}-\delta_{ij})$$

$$\begin{aligned}<\psi_{k\to s}|\hat{H}|\psi_{k\to s}>=2\sum_{m}^{n}\varepsilon_m+(\varepsilon_s-\varepsilon_k)+&\\ \sum_{m}^{n}\sum_{l}^{n}(2\gamma_{ml}-\delta_{ml})-&\\ \sum_{l=1}^{n}[(2\gamma_{kl}-\delta_{kl})-(2\gamma_{ls}-&\\ \delta_{ls})-\gamma_{ks}+2\delta_{ks}]&\end{aligned}$$

$$<\psi_G|\hat{H}|\psi_{k\to s}>=\sqrt{2}\,\{\varepsilon_{ks}+\sum_{m=1}^{n}[2(mm|ks)-(mk|sm)]\}$$

$$<\psi_{k\to s}|\hat{H}|\psi_{l\to r}>=2(lr|ks)-(lk|sr)$$

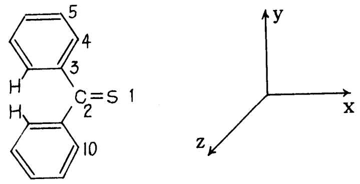
$$\begin{aligned}<\psi_{k\to s}|\hat{H}|\psi_{k\to r}>=\varepsilon_{rs}+\sum_{m=1}^{n}[2(mm|rs)-(mr|sm)]+&\\ 2(kr|sk)-(kk|rs)&\end{aligned}$$

$$\begin{aligned}<\psi_{k\to s}|\hat{H}|\psi_{l\to s}>=-\varepsilon_{lk}-\sum_{m=l}^{n}[2(mm|lk)-(ml|km)]+&\\ 2(ls|ks)-(lk|ss)&\end{aligned}$$

The coefficients, *c's*, used to calculate the above integrals were the self-consistent ones and the two-center electron repulsion integrals were calculated using the Nishimoto-Mataga relation.[18)] The computations were performed on IBM-370 computer using INDO-program obtained from QCPE center, to which a CI subroutine was added.

Results and Discussion

Conformational Analysis of Thiobenzophenone. The hexagonal nature of benzene imposes a steric hindrance on the planarity of the molecule. Ortho-ortho-hydrogen interaction will prevent the coplanarity of the two benzene nuclei. The extent of this steric effect is best investigated through the calculations of the total energy of the molecule as a function of angle of rotation of one of the benzene nuclei. The results help one to predict whether the molecule is a "free rotor," rigid or a "quasi-rigid" one. The total energy is calculated by MO calculations using the INDO procedures.



(a)

Previous electronic structure calculations were reported on S-containing compounds[19–21)] excluding the contribution of the 3d sulfur atomic orbitals. In an ab initio calculation,[22)] it has been shown that the 3d's orbitals of sulfur play a very minor role in the population analysis (and hence in bonding) as has been reported before.[23–27)]

In this work, MO computations were performed neglecting the 3d sulfur atomic orbital. The configuration adopted (a) for the molecule is shown, bond length and bond angle were taken from the literature.[9)] Molecular orbital calculations were performed on the planar conformer as well as nonplanar conformers whereby one of the benzene rings is rotated 15, 30, 45, 60, and 90° around the C_2-C_3 axis. A comparison of the total energy, dipole moment, energy of the lowest electronic transition and the oscillator strength is given in Table 1. The lowest electronic transition is forbidden (f=0.0, HOMO is "n+σ" and LUMO is π^*)

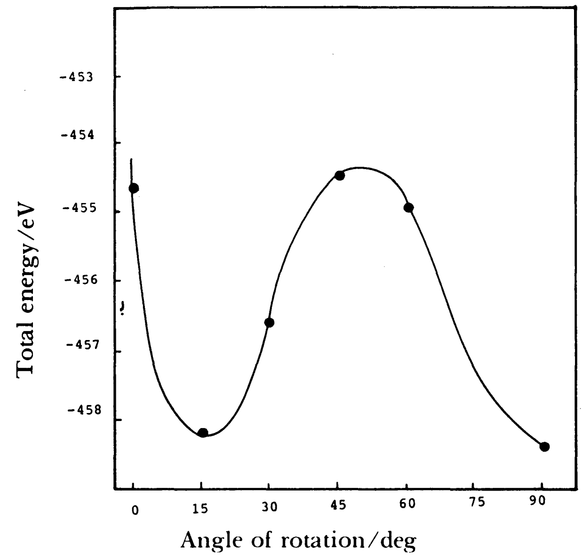


Fig. 1. Variation of INDO-total energy of thiobenzophenone with the angle of rotation of one of the benzene rings.

Table 1. Variation of Total Energy, Dipole Moment, and Transition Energy with Thiobenzophenone Geometry

Angle of rotation/°	Total energy/eV	Dipole moment/D	Lowest transition K/eV	Osc. Str.
0	−454.62	4.08	3.08 3.48	0.00 0.10
15	−458.20	7.40	3.37	0.16
30	−456.59	7.36	4.02	0.30
45	−454.45	6.92	3.73	0.18
60	−454.92	6.36	4.83	0.27
90	−458.39	5.99	3.25 4.29	0.00 0.35

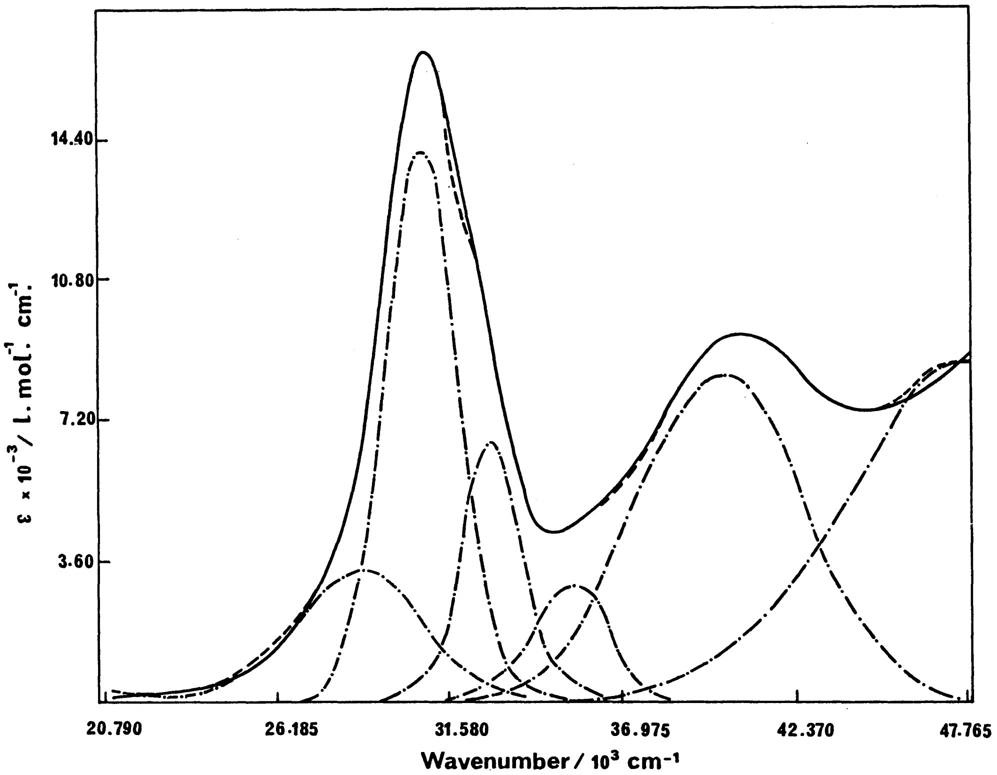


Fig. 2. Electronic absorption spectrum of thiobenzophenone in ethanol. ——: Exp. spectrum, —·—·—: Gausian component bands, ––––: fitted spectrum when not coincident with experimental.

for the planar as well as the perpendicular conformer. For other conformers, mixing of orbitals does not permit the calculation of pure n(n+σ)→π* transitions. The variation of the total energy of thiobenzophenone with the angle of rotation is shown in Fig. 1. The height of the barrier to internal rotation is of the order of 4 eV indicating that the molecule is not a free rotator. INDO procedures give good results for calculated ground state energy but not as good for the excited states. Generally, calculated energies by the INDO method are slightly higher than those calculated by other more accurate procedures. Results of this work indicate that the most stable conformer of thiobenzophenone has an angle of 15° between the planes of the benzene rings. The lowest π→π* transition energy (3.37 eV) agrees satisfactory with experiment. Gaussian analysis was performed and the lowest electronic transition was found at 3.56 (in ethanol) and at 3.81 eV (in cyclohexane) Fig. 2.

Dipole moment measurements of a series of thioketones have shown that compounds in which thiocarbonyl group is not subjected to conjugative or resonance effects have smaller dipole moments than the corresponding ketones. This indicates that the polarity of the thiocarbonyl group is considerably smaller and possibly reversed compared with that of C=O group.[28,29] On the other hand, thioketones in which intramolecular perturbation of the C=S group is possible (for example within the aromatic series) have dipole moments which indicate a higher polarizability for C=S than for the C=O. Table 2 compares some experimental results of dipole moments measured in benzene at 20 °C.[30,31]

Table 2. Experimental Values of Dipole Moments of Some Carbonyl and Thiocarbonyl Compounds in Benzene at 20 °C

Compound	C=S	C=O
Thiobenzophenone	3.37	2.95
4,4′-Dimethylthiobenzophenone	3.45	3.45
4,4′-Dimethoxythiobenzophenone	4.44	3.90
4,4′-Bis(dimethylamino)-thiobenzophenone	6.12	5.16

Data are from Refs. 23 and 24.

Table 1 gives the calculated dipole moment for thiobenzophenone whereas Table 3 gives the dipole moments of substituted thiobenzophenones. The calculated dipole moments are only slightly higher than the experimental ones for thiobenzophenone and 4,4′-dihydroxy derivative but seems to be significantly higher for 4,4′-diaminothiobenzophenone. These effects are direct results of the method of calculation, parameterization, and configurations adopted. The dipole moments lie along the C_{2v} symmetry axis and are strongly dependent upon the orientations of the lone pair of electrons. Consequently, rotating one of the benzene nuclei of thiobenzophenone alters signifi-

Table 3. Comparison of the Calculated Dipole Moments and Total Energies of Some Substituted Thiobenzophenones

Compound	Dipole moment/D	Total energy/eV
Thiobenzophenone	4.08	−454.62
4-Aminothiobenzophenone	4.26	−554.38
4-Hydroxythiobenzophenone	5.59	−676.15
4,4′-Dihydroxythiobenzophenone	4.65	−900.30
4,4′-Diaminothiobenzophenone	10.41	−571.74
4-Amino-4′-hydroxythiobenzophenone	2.85	−778.48

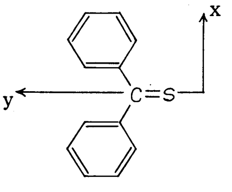
Table 4. Variation of the Net Charge Density on Certain Atoms of Thiobenzophenone as a Function of the Angle of Rotation

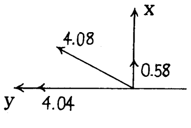
Angle of rotation	S_1	C_2	C_4	C_5	C_{10}	C_{11}
0	−0.0349	0.2581	−0.1063	−0.0688	−0.1245	−0.0727
15	−0.1436	0.2116	−0.0189	−0.0382	−0.1499	−0.0852
30	−0.1333	0.1910	−0.0060	−0.0266	−0.1343	−0.0966
45	−0.1404	0.2090	−0.0085	−0.0121	−0.1349	−0.0951
60	−0.1456	0.2302	−0.0190	−0.0124	−0.1351	−0.0949
90	−0.1498	0.2452	−0.0263	−0.0137	−0.1363	−0.0939

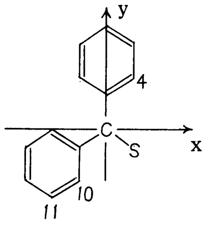
cantly the value of calculated dipole moment.

The calculated dipole moments of substituted thiobenzophenones reveal some important results. Generally, substitution by one or two hydroxyl, one or two amino groups increases the dipole moments and increases the polarization of the thiocarbonyl group. However, the calculated dipole moment of 4-hydroxyl-4′-aminothiobenzophenone is significantly smaller than that of the thiobenzophenone. Hence, the -OH and -NH_2 groups have acted in opposite directions with a net result of decreasing the polarizability of the C=S.

The reactivity of a molecule can nicely be correlated with the charge density of the different sites of the molecule whereas the algebraic signs of the coefficients of the AO's constituting the HOMO and LUMO are directly concerned with the pathway of a chemical reaction. In Table 4 one compares the charge densities on the active sites of the molecule (S_1, C_2, C_4, C_5, C_{10}, C_{11}) in the different conformers. We cannot compare the coefficients of the MO's of the different conformers since rotation mixes the different orbitals on the benzene rings. The data in Table 4 indicates some interesting results. The thiocarbonyl group (C=S) has only a slight effect on the reactivity of the benzene rings since no pronounced excess of negative or positive charges is calculated on the different atoms. However, thiobenzophenone is a dipole with calculated moment of 4.08D (planar conformer) compared with the experimental 3.37D. The components of the dipole moment (in Debye) are: u_x=0.58, u_y=4.04, and u=4.08 (0.83 atomic and 3.34 polarization). The dipole moment vector is directed from the C=S to the benzene rings. In other words, there is a net built of negative charge on the benzene rings and one can say that the C=S group activates, though slightly, the molecule. The calculated dipole moment, 7.04D, for the most stable conformer of thiobenzophenoe is remarkably higher than the experimental one. This is probably due to the method of calculations used in this work. INDO procedures lead to relatively higher values of dipole moment, even for the planar conformer. The slight net negative charge on S-atom explains the role of C=S in cycloaddition.







It is interesting to correlate the charge density, on the benzene rings, to the angle of rotation of one of the benzene nuclei aroun the y-axis (b). As the results in Table 4 indicates, the rotation of the benzene ring led to excess of charge density on the S-atom and a lack of the rotating benzene ring from charge density. On the other hand, there has been an increase of charge density on the non-rotating benzene ring (C_{10}).

Rotation of one of the benzene rings is expected to affect the calculated value of the dipole moment. The lowest value of dipole moment, 4.08 D, is computed for the planar conformer whereas the highest value, 7.40 D, is computed for the perpendicular conformer. Rotation of the plane of the benzene ring by 15° almost doubles the dipole moment.

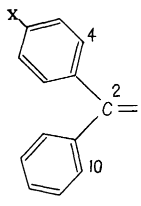
Electronic Structure of Substituted Thiobenzophenones. INDO-molecular orbital calculations were

Table 5. Net Charge Density and Coefficients of the HOMO and LUMO of the Studied Thiobenzophenones (TBP)

Compound	S_1	C_2	C_4	C_5	C_{10}	C_{11}
TBP	−0.0349[a)] −0.2487[b)] 0.2476[c)]	0.2581 0.6492 −0.0081	−0.1063 −0.2638 0.0979	−0.0688 −0.0972 0.1533	−0.1245 −0.2349 −0.4359	−0.0727 −0.0946 0.1533
4-Amino-	−0.0305 −0.0173 −0.2454	0.2512 0.0297 0.6512	−0.0887 −0.0898 −0.2558	−0.0911 0.1506 −0.1024	−0.1037 −0.1823 −0.2297	−0.0944 −0.5445 −0.0801
4-Hydroxy-	−0.0366 −0.0083 0.2458	0.2581 0.0221 −0.6468	−0.1143 −0.0265 0.2642	−0.0623 0.1728 0.1016	−0.1123 −0.2778 0.2285	−0.0957 −0.5974 0.0752
4,4′-Dihydroxy-	−0.0390 0.0264 0.2444	0.2449 −0.0231 −0.6496	−0.0894 −0.1301 0.2517	−0.1170 0.2361 0.0725	−0.0987 0.0269 0.2238	−0.1051 −0.3220 0.0808
4,4′-Diamino-	−0.0428 0.3620 −0.3768	0.2761 −0.0221 0.2452	−0.1977 0.0341 0.1824	−0.2807 0.0323 −0.0983	−0.1034 −0.2425 0.0206	−0.1100 −0.1757 −0.1817
4-Hydroxy-4′-amino-	−0.0344 0.0203 0.2405	0.2558 −0.0193 −0.6442	−0.1068 −0.1288 0.2526	−0.1139 0.2291 0.0739	−0.1211 0.0490 0.2303	−0.0821 −0.3003 0.0849

a) The values on the first line represent the net charge density. b) The values on the second line represent the coefficients of the HOMO. b) The values on the third line represent the coefficients of the LUMO.

performed on a series of 4,4′-disubstituted thiobenzophenone in order to correlate the reactivity of these compounds to the calculated parameters and to compare the reactivity of the different compounds. Computations were performed on the planar conformers only and Table 5 summarizes some of the calculated parameters for different substituted thiobenzophenone; those of thiobenzophenone are included for comparison. It is noticed that the net negative charge on S-atom is the highest in 4,4′-diamino derivative, it is high in 4-hydroxy- and 4,4′-dihydroxythiobenzophenones than it is in thiobenzophenone. The oxygen and nitrogen atoms of the substituents are σ-acceptor and π-donors[22)] but they did not lead to a decrease of the charge density on S-atom. Substitution by -OH or $-NH_2$ groups has not led to a built up of negative charge density than in the case of thiobenzophenone. The highest charge density (in hydroxy- or aminothiobenzophenone) is on C_4 and C_{10}.



The numerical values of the coefficients of AO's forming the HOMO and LUMO are dependent on the

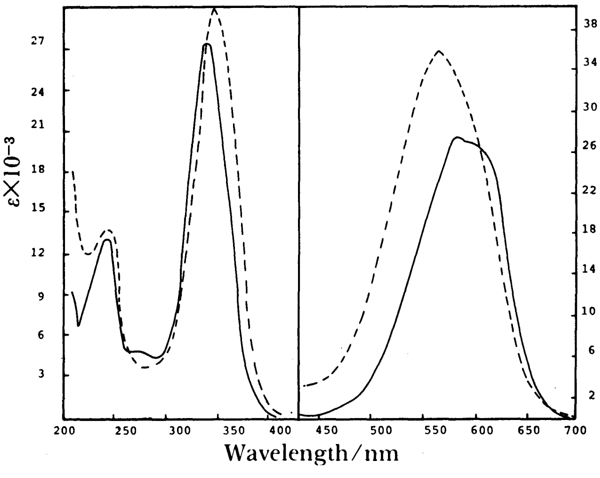


Fig. 3a. Electronic absorption spectra of 4,4′-dimethoxythiobenzophenone.
——: In cyclohexane, ----: in ethanol.

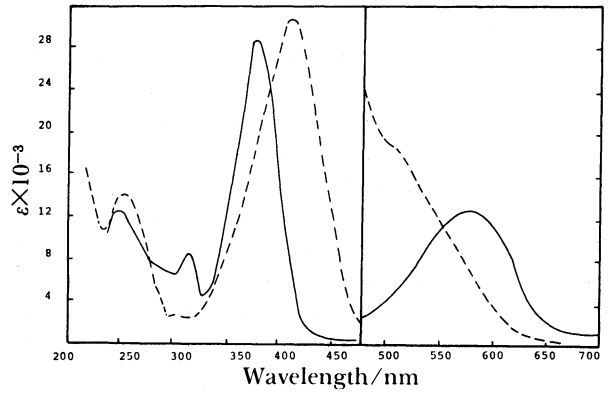


Fig. 3b. Electronic absorption spectra of 4,4′-diaminothiobenzophenone.
——: In carbon tetrachloride, ----: in ethanol.

Table 6. Analysis of the Absorption Spectra of Thiobenzophenone in Different Solvents

Solvent / parameter	Ethanol			Cyclohexane		
	$\bar{\nu}_{\max}/\mathrm{cm}^{-1}$	ε	f	$\bar{\nu}/\mathrm{cm}^{-1}$	ε	f
	30780	13950	0.17	32040	9600	0.10
	39990	8060	0.23	40440	9250	0.39
	47700	8460	0.34	30760	7600	0.12
	32860	6300	0.06	47830	6360	0.14
	28740	3200	0.07	33330	1590	0.01
	35340	2670	0.03	34480	2560	0.03

Table 7. Analysis of the Absorption Spectra of Some Thiobenzophenones in Cyclohexane

Compound	$\bar{\nu}_{\max}/\mathrm{cm}^{-1}$	ε	f
4-Methoxy-4′-ethoxy-	29500	31190	0.44
	40728	17720	0.48
	47770	18600	0.67
	33118	9890	0.15
	36190	7000	0.08
	26850	3410	
4,4′-Diethoxy-	29210	27410	0.20
	30480	20700	0.16
	40860	20770	0.49
	28040	13430	0.10
	47040	19030	0.42
	32900	8010	0.11
	35890	6810	0.11
	27240	6500	0.11
4,4′-Dimethoxy-	29600	24360	0.29
	41490	8060	0.14
	48530	5620	0.03
	45170	7950	0.23
	31710	6000	0.05
	35160	4710	0.24
	27750	4930	0.05
4,4′-Diamino-[a)]	26670	27880	0.41
	40270	11430	0.31
	33360	6250	0.25
	31690	2660	0.01
4,4′-bis(Dimethylamino)-[a)]	23990	37970	0.30
	25371	19170	0.16
	38930	18500	0.76
	29330	7220	0.04
	30850	10280	0.12
	27110	10010	0.14
	22710	5830	0.03
	32800	4550	0.05

a) Using carbon tetrachloride as a solvent.

Table 8. Comparison between Calculated and Experimental Transition Energy and Oscillator Strength

Compound	Exp. (G.analysis)		Calcd	
	ΔE/eV	f	ΔE/eV	f
Thiobenzophenone	3.81	0.12	3.48	0.09
	3.97	0.10	3.60	0.00
	4.13	0.01	(a)4.03	0.27
	4.28	0.03	4.60	0.00
	5.01	0.39	5.61	0.00
	5.93	0.14	6.30	0.30
			3.37	0.35
			(b)4.11	0.17
			4.46	0.17
			5.68	0.31
			6.01	0.22
4,4′-Dimethoxy-	3.44	0.05	3.26	0.00
	3.67	0.30	(c)3.49	0.34
	3.93	0.05	3.53	0.15
	4.36	0.24		
	5.14	0.14	5.74	0.50
	6.02	0.03		
4,4′-Diamino-	3.33	0.14	3.11	0.00
	3.92	0.01		
	4.14	0.25	4.17	0.00
			4.77	0.00
	4.98	0.31	4.94	0.17
			5.20	0.41
4-Amino-4-hydroxy-			3.02	0.00
			3.15	0.00
			3.44	0.14
			4.00	0.36
			5.55	0.52
4-Amino-			3.46	0.12
			3.62	0.33
			3.69	0.74
			4.95	0.00
			5.94	0.01
			6.07	0.56
4-Hydroxy-			3.08	0.00
			3.49	0.12
			3.69	0.96
			4.96	0.00
			5.08	0.00
			5.98	0.05
			6.09	0.53

a) Planar conformer. b) An angle of 15° between the planes of benzene rings. c) Data are for 4,4′-dihydroxythiobenzophenone.

type of the substituent (Table 5). In the case of 4-aminothiobenzophenone the coefficient of S-atom is −0.0173 compared to −0.2487 in thiobenzophenone in the highest occupied molecular orbital (HOMO) and is −0.2454 compared to +0.2476 in thiobenzophenone (in the LUMO). Characteristic variations of the coefficients and the net charges are seen for the different atoms in the different MO's as indicated in Table 5.

Spectral Analysis. The electronic absorption spectra of some thiobenzophenones have been reported.[32)] The observed bands correspond to highly overlapping transitions (Figs. 3a, b). In order to resolve the individual band parameters a curve analysis has been carried out.[33,34)] The electronic absorption spectra were analyzed, using the Gaussian line shape, as shown in Fig. 2 for thiobenzophenone. The resolution of the observed absorption spectrum into its components is used to determine the appropriate values of the parameters as indicated in Tables 6 and 7. Gaussian analysis shows that there are other transitions taken place underneath the two ultraviolet absorption bands observed experimentally. Such transitions are characterized by low oscillator strength, hence the parameters observed are not quite real due to the overlap of the transitions. Also, it is clear that the band parameters of the experimental curve are affected by both changing the medium and/or the substituent.

Comparison with Experiment. A comparison of the computed transition energy and oscillator strength with those obtained after Gaussian analysis of the spectra of some thiobenzophenones is given in Table 8. Many computed transitions are theoretically forbidden yet they are observed experimentally with weak intensity. From both the experimental and theoretical results it is clear that the spectral band corresponds to a number of overlapping transitions. This overlapping causes inaccuracy in the experimentally calculated oscillator strength and is the reason of the observed discreapancy between the calculated and experimental values. On the other hand, the correspondence between the calculated and experimental transition energies.

Conclusion

The method of calculations used in this work, INDO-CI, proved to be a satisfactory method in explaining and predicting the electronic structure of the studied thiobenzophenones. It has been shown that the most stable conformer of thiobenzophenone is nonplanar with an angle of 15° between the planes of the benzene rings. The height of the barrier to internal rotation is of the order of 4 eV revealing that the molecule is not a free rotator.

Calculations of the charge density and dipole moment led to some important conclusions. Generally, substitution in the benzene rings of thiobenzophenone resulted in an increase in the dipole moment except in the case of 4-hydroxy-4′-aminothiobenzophenone which has a dipole moment lower than the parent compound. This result indicates that the polarization of the C=S group has been diminished or even reversed in this compound. For the studied compounds there has been a net built up of charge density on the benzene rings, hence increasing the activity.

The experimental results of photocycloaddition of thiobenzophenone to substituted olefins[11–14] go along with the theoretical predictions of this work especially for the mechanism of nucleophilic attack of thiobenzophenone on the olefins and the formation of thietane derivatives. The calculated charge densities on C_2 and S_1 as well as their coefficients in the HOMO (Table 5) favors the polar addition of the olefins to the thiocarbonyl group.

No data is available on the reactivities of substituted thiobenzophenones. The results in Table 5 predict that substitution in the thiobenzophenone will affect its reactivity.

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