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THE PHOTOELECTRON SPECTRA OF 4-METHYLENE THIACYCLOHEXANE DERIVATIVES THROUGH-BOND INTERACTION

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Abstract—The photoelectron spectra of 4-methylene thiacyclohexane, 4-difluo romethylene thiacyclohexane and *trans*-2-methylene-6-thiaperhydronaphthalene are described and compared with thiacyclohexabne, difluoromethylene-cyclo hexane and *cis*-2-methylene-6-thiaperhydronaphthalene.

A through bond interaction between the sulphur lone pair and the vinyl-π-system is observed. The results are discussed in relation with the sigma-coupled transition observed in the electronic absorption spectra of the dicyano methylene derivatives by P. Pasman.

INTRODUCTION

Throughbond interaction[1,2] between non-conjugatively connected π- or lone pair electron systems has been studied by photoelectron spectroscopy. Most cases described the interaction between identical groups. We are currently studying through bond interaction between non-equivalent groups[3,4,5] by P.E. spectroscopy and ultra-violet absorption- and emission spectroscopy.

The through-bond interaction between a π-electron system with electron acceptor properties and a π- or n-electron system with electron donor properties separated by three or five sigma bonds leads to the occurrence of the so-called "sigma coupled transition" as shown by Pasman.[5,6] This paper reports the observation of such interaction by photo-electron spectroscopy over three and for the first time even over five sigma bonds between the sulphur lone pair system (n_s) and a π-system in compounds **1b**, **1c** and **4a** (see Fig. 1).

Furthermore semi-empirical calculations (MIEHM and MINDO/3) were carried out to support these experimental results. The chair form is the most stable conformation for all compounds under investigation, as is evidenced either by direct conformational studies (**1a**, **2a**, **2b**, **3a** and **3d**)[7-11] or by comparison with

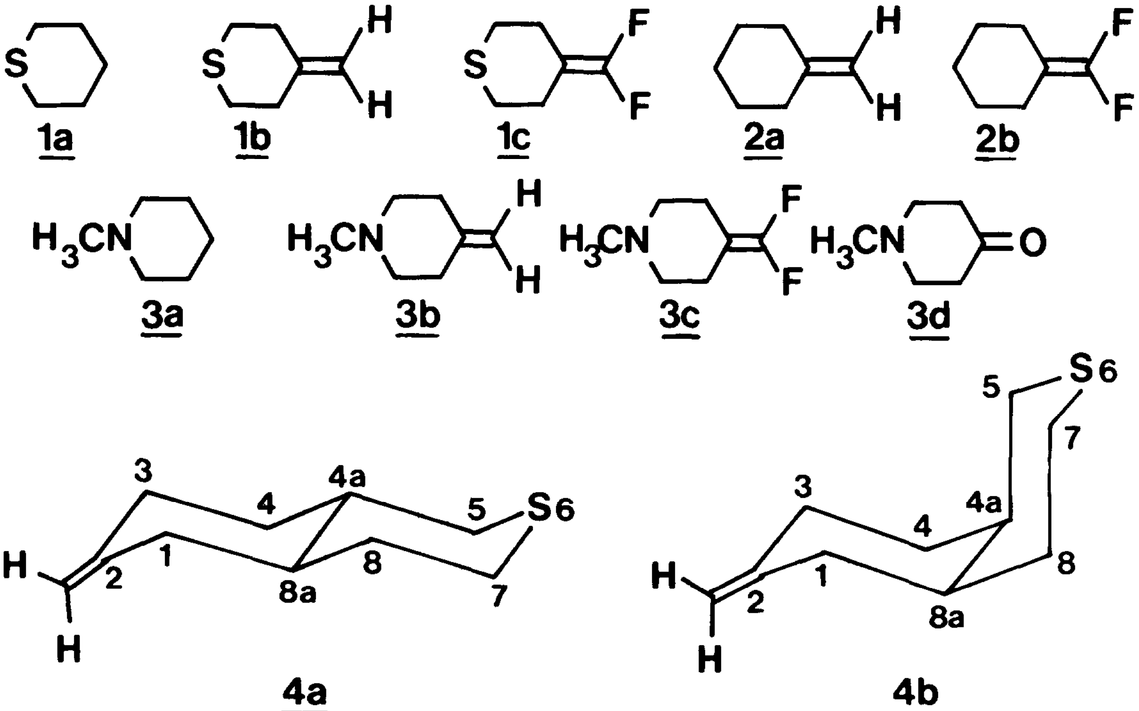

Fig. 1.

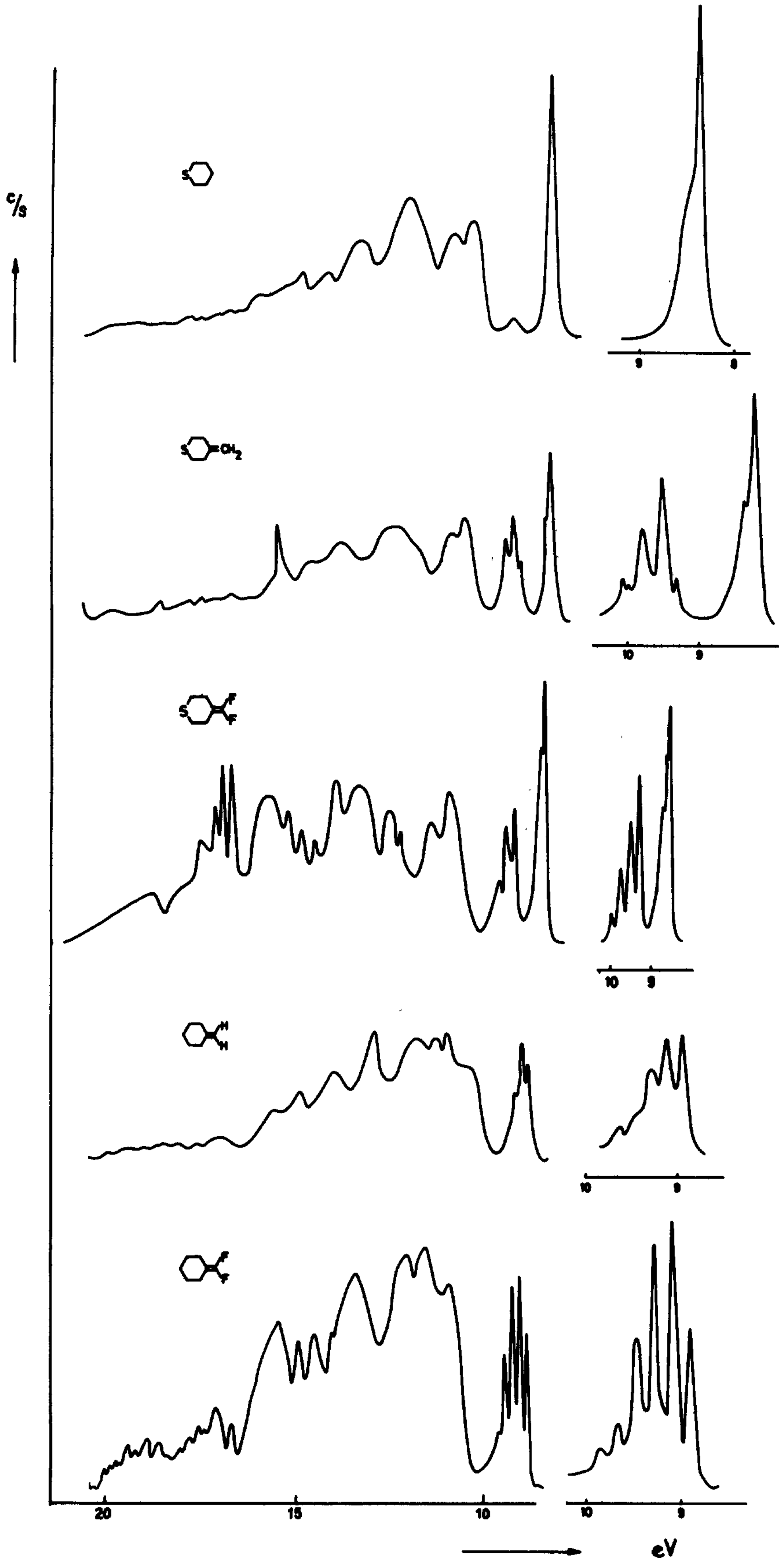

Fig. 2.

related compounds of known conformation (**1b**, **1c**, **3c**, **4a** and **4b**).[8,13] The results of the calculations mentioned above are in full agreement with this preponderance of the chair-conformation. For the evaluation of the throughbond interaction in the monocyclic systems, **1b** and **1c**, the following reference compounds have been measured (see Fig. 1): thiacyclohexane (**1a**), methylene-cyclohexane (**2a**) and difluoro methylene cyclohexane (**2b**), while for **4a** the non-coupled isomer **4b** is used as reference.

RESULTS

1. *Cyclohexane Dervatives*

The He (I) photoelectron spectra of **1a**, **1b**, **1c**, **2a** and **2b** are shown in Fig. 2 along with expanded spectra of the outer n and π bands. The first band in the spectra of the compounds **1a**, **1b** and **1c** can be attributed to ionization from an orbital which has mainly lone pair character and is oriented perpendicular to the C–S–C plane ($n_\perp$).[14] This band shows a vibrational component of 600 cm^{-1}, which can be assigned to the C–S stretching vibration. The first band in the spectra of compounds **2a** and **2b** can be attributed to the π system. This band possesses a well resolved vibrational fine structure with a frequency of 1450 cm^{-1}, which can be assigned to the ionic C=C– stretching vibration.

The bifunctional derivatives **1b** and **1c** have the symmetry C_s. The $n_\perp$ sulfur lone pair and the ethylene π orbital are of the a′ symmetry and can in principle be coupled through-bond via σ_{C-C} orbitals of the same symmetry. The occurrence of this through-bond coupling is supported by the increasing difference in ionization energy between the bands attributed to the lone pair and π ionization as compared with these processes in the monofunctional compounds, **1a** and **2a** resp. **1a** and **2b**, see Fig. 3 and 4. The through-bond interaction is expected to lead to a small destabilisation of the upper occupied orbital and a stabilisation of the lower occupied orbital interacting through-bond.[3]

We have to account for inductive effects of the substituents. Substitution of an atom or group by one of higher electronegativity results in a stabilization of the other orbitals. The inductive and through-bond effects are opposed for the first orbital. The inductive effect of the π system on the n system, and v.v., can in principle be estimated by measuring the energy of the nitrogen lone pair n_N and the π system in the compounds **3a**, **3b**, **3c** and **3d**. Through-bond interaction in the last three compounds can be excluded because the nitrogen lone pair is perpendicular to the σ system. The photoelectron spectra of **3a**, **3b** and **3d** are given in Fig. 5. From Fig. 6 we can deduce that the inductive effects can be neglected for substitution of the 4-CH_2 group by $C{=}CH_2$; for substitution by a C=O group the inductive effect gives a stabilisation of the n_N system of 0.42 eV. The increase of the IP of an electron located on the N atom under influence of a dipole can be calculated using a field model.[15]

$$\Delta IP = \frac{14.39}{\varepsilon}\left(\frac{1}{R_{CN}} - \frac{1}{R_{ON}}\right)\frac{\mu_{CO}}{4.8R_{ev}}$$

$\varepsilon = 2$ (effective dielectric constant).

Using the presence of a C=O dipole of 2.8 Debye[16] the calculated increase of the IP is $\Delta IP = 0.35$ eV, which is in reasonable agreement with the observed increase of 0.42 eV.

Where the preparation of the $C{=}CF_2$ derivative **3c** gives insurmountable problems, it was not possible to measure the photoelectron spectrum and to deduce the inductive effect of the $C{=}CF_2$ group.

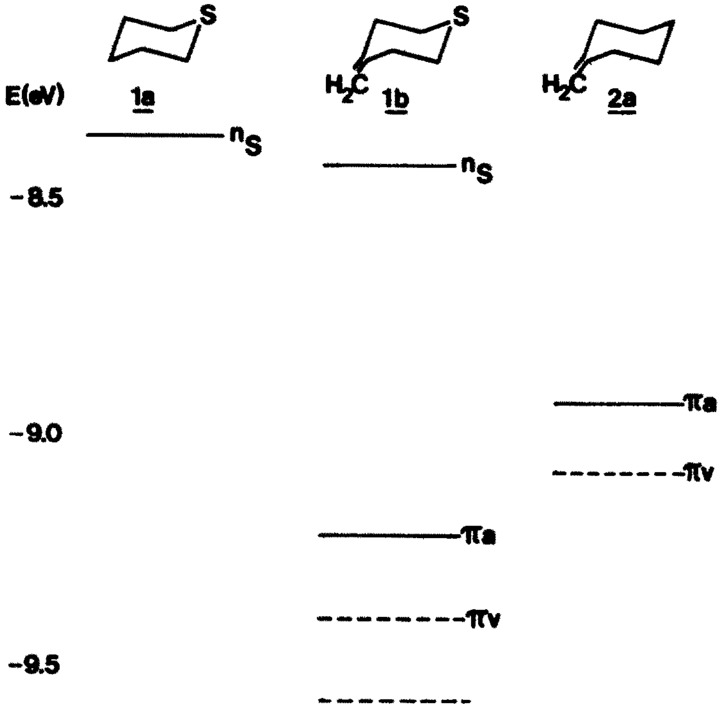

Fig. 3. Correlation of upper occupied levels in **1a**, **1b** and **2a** as determined by PE-spectroscopy.

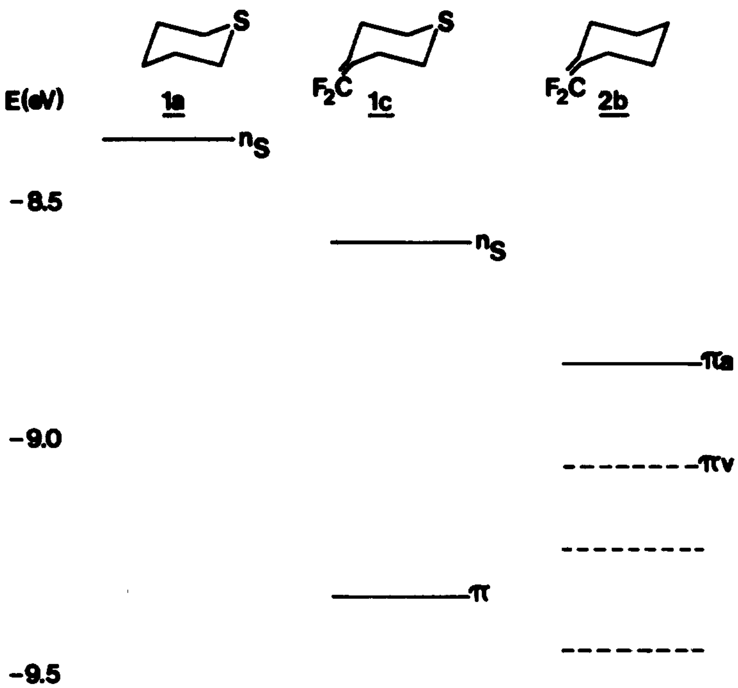

Fig. 4. Correlation of upper occupied levels in **1a**, **1c** and **2b**.

A field-model calculation of the increase of the IP of a lone pair electron under influence of the C=CF$_2$ dipole gives an effect of $\Delta IP = 0.15$ eV, using a C=CF$_2$ dipole of 1.27 Debye.[17] This is also substantiated by the MIEHM[19] calculations of **1c** and **3c** which predict an increase of $\Delta IP = 0.18$ eV for the sulphur lone pair ($n_\perp$) level due to the inductive effect.

2. *Perhydronaphthalene Derivatives*

Compounds **4a**, *trans*-2-methylene-6-thiaperhydronaphthalene and the *cis* isomer **4b** were synthesized, their He (I) photoelectron spectra are shown in Fig. 7.

The first band in these spectra, IP$_a$: 8.26 eV, resp. 8.22 eV can be attributed to the S lone pair ($n_\perp$) in reasonable agreement with the value of 8.36 eV in thiacyclohexane. This band has a vibrational component in both spectra of 960 cm^{-1}. The second band in both spectra shows a well developed vibrational structure with IP$_a$: 9.03 eV for the trans compound, resp. IP$_a$: 8.95 eV for the *cis* compound. This band can be assigned to ionization of the π system. Remarkable is the change in the vibrational envelope in this band. The O–O transition of the π band of compound **4a** is the most intense, and the vibrational energy on the ionic state (1520 cm^{-1}) is very similar to that of the ground state molecule (1640 cm^{-1}). This contrasts with the behaviour of the π band of compound **4b** where the O–1 transition is the most intense and the vibrational energy in the ionic state is 1250 cm^{-1}. The same holds for the compounds **1b** resp. **2a** and **2b**. These differences in the vibrational structure can be explained by assuming that in the compounds with a through-bond coupling the π orbital is more delocalized, making that the influence of ionization of the π-electrons on the bond strength is relatively small and that the internuclear distance in the corresponding ion very similar to that of the molecule.

CALCULATIONS

MINDO-3[18] and MIEHM[19] MO-calculations were carried out. To calculate the energy of these compounds it was necessary to extend the programs to a capacity of 75 atomic orbitals. Molecular coordinates were taken from the literature.[20] The MINDO-3 program incorporates a geometry optimisation. From the results of the geometry optimisation it can be concluded that the chair form is the most stable conformation for this type of molecules. For the MIEHM calculations these optimialized geometries have been taken. In Table 1, the experimental and the calculated I.P. for the lone pair and π system are collected. There are several discrepancies between the calculated and experimental values. The values of MIEHM calculated I.P.'s are 2.0–2.5 eV higher than the observed values. In Fig. 8 the MIEHM lone pair and π energies are plotted against experimental energies as indicated in Table 1.

It is evident that the nitrogen lone pair level must be treated separately; the reason for this is believed to be a different deviation from Koopman's theorem. The discrepancy in the calculated energies of the π systems of the fluorinated derivatives can be explained by assuming that the parametrization is not suitable to correct for the strong inductive effect of the fluorine atoms. The correlation between calculated orbital energies and the experimental ionization energies gives a consistent interpretation of the first bands in the photoelectron spectra.

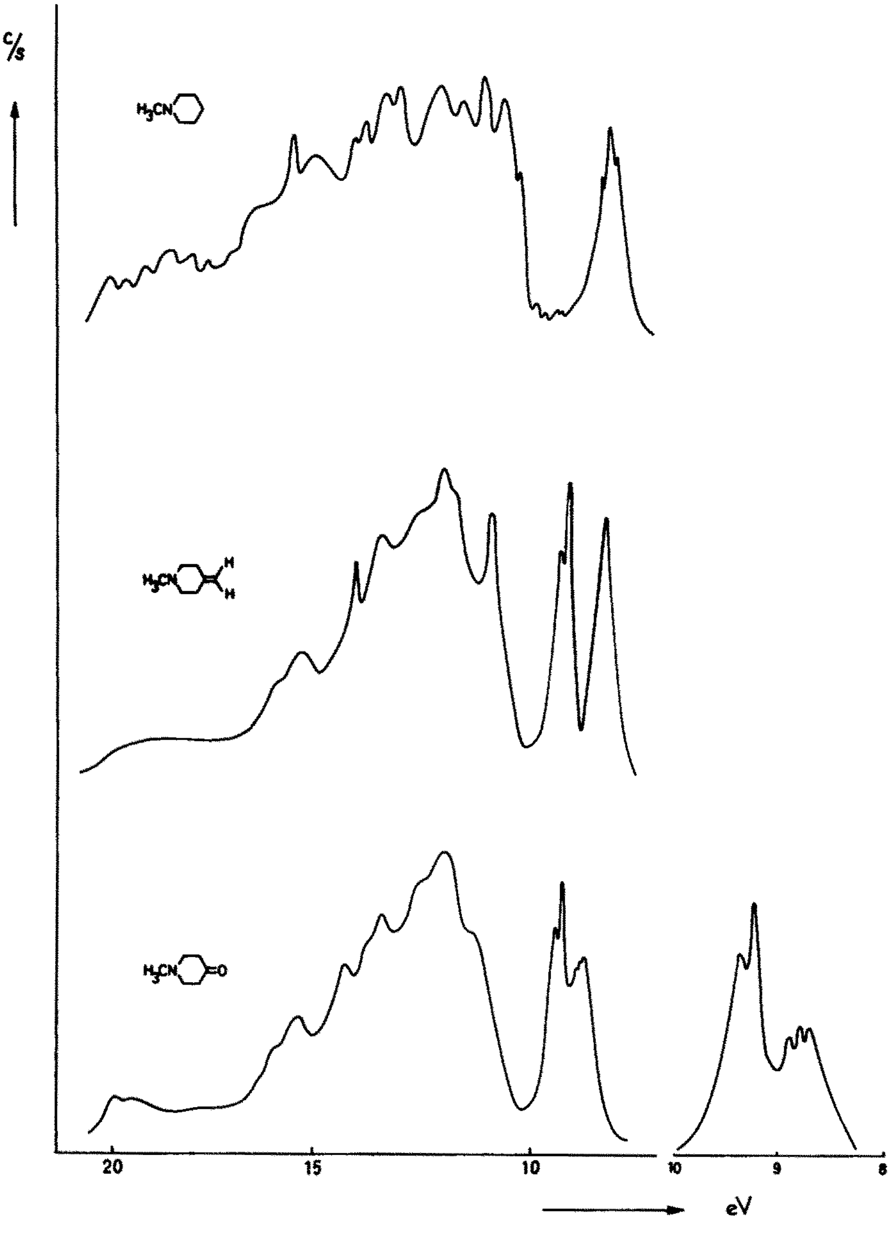

Fig. 5. No subscript.

DISCUSSION AND CONCLUSIONS

Cyclohexane derivatives

The difference between the lone pair sulfur ($n_\perp$) and the π level of the monofunctional reference compounds **1a** resp. **2a** is 0.57 eV. In the bifunctional system **1b** the corresponding splitting is significantly increased (0.80 eV) due to a rather strong (0.29 eV) stabilization of the π-level and a concomitant small (0.06 eV) stabilization of the $n_\perp$ level. Since the influence of the inductive effect of the π-system on the $n_\perp$ system and v.v. can be neglected—vide supra—and also changes in conformation of **1b** relative to **1a** and **2a** are minor the strongly increased level splitting in **1b** is presumably due mainly to through-bond interaction. A simplified treatment of through-bond interaction in **1b** invokes the interaction of the $n_\perp$ and π-orbital via a single σ orbital of proper symmetry, while in **1a** and **2a** a σ-orbital of comparable energy is assumed to interact with only $n_\perp$ or π-orbital respectively. From such a treatment significant stabilization of π in **1b** relative to **2a** is predicted—as observed—but at the same time a slight destabilization of $n_\perp$ in **1b** to **1a** is predicted.[3] The latter is in invariance with the experimentally found slight (0.06 eV) stabilization. Apparently the prediction of the crude three orbital model for through-bond interaction is too imprecise to account for such minor effects, which are however rather well predicted by the MIEHM calculation that shows a stabilization of 0.10 eV for the $n_\perp$ level in **1b** as compared to **1a**.

For the fluorinated derivative **2b** the I.P. of the π-level amounts to 9.06 eV. From the results of the MIEHM calculations of **1c** and **3c** as well from the

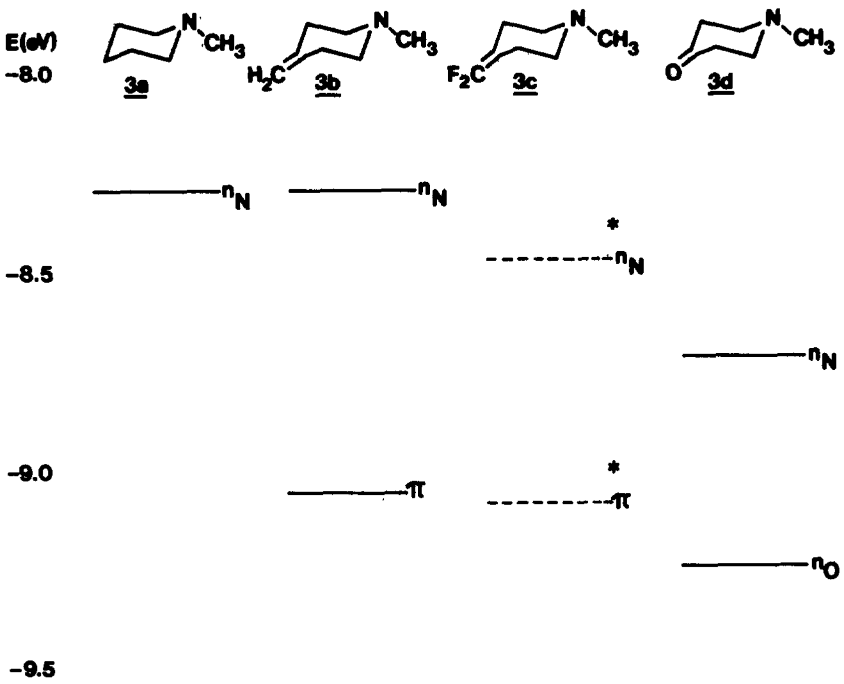

Fig. 6. Correlation of upper occupied levels in **3a**, **3b**, **3c** and **3d** as determined by PE-spectroscopy.

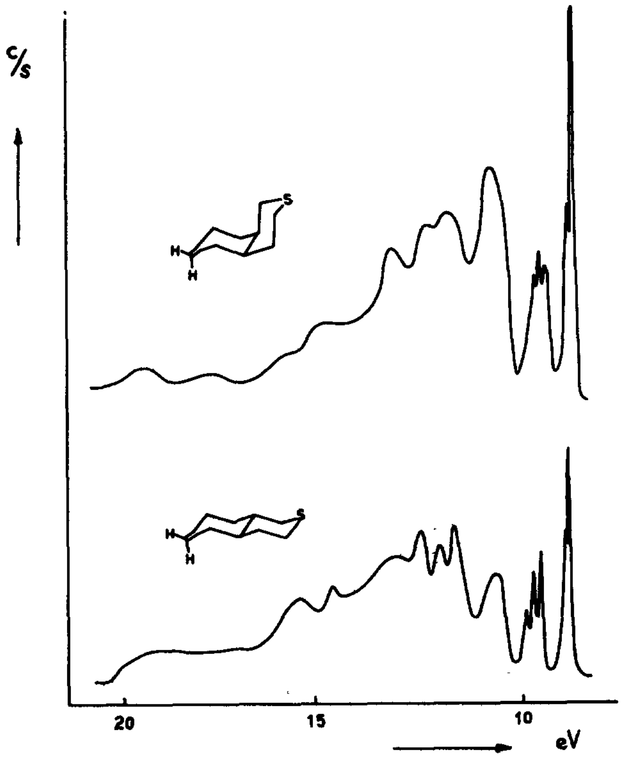

Fig. 7. No subscript.

Table 1. Experimental IP's and calculated ε's

		Exp.		MIEHM	MINDO-3
		IP_a	IP_v		
1a	n(S)	8.36	8.36	10.82	9.07
	n(S)		8.42	10.92	8.93
1b	π	9.22	9.40	11.63	9.67
	n(S)		8.58	11.57	
1c	π	9.34	9.34	12.97	
2a	π	8.93	9.08	11.32	9.40
2b	π	8.84	9.06	12.70	9.28
3a	n(N)		8.29	10.31	8.57
	n(N)		8.29	10.22	8.30
3b	π	9.05	9.05	11.50	9.64
	n(N)		8.47"[1]	10.92	8.53
3c	π	9.08"[1]		12.83	9.47
3d	n(N)		8.71	10.60	8.69
4a	n(S)		8.26	10.82	8.84
	π	9.04	9.23	11.39	9.67
4b	n(S)		8.22	10.85	8.92
	π	8.95	9.10	11.50	9.42

[1] Calculated from MIEHM-results.

field-model calculation it follows that an increase of the ionization energy of the sulphur lone pair ($n_\perp$) orbital of ΔIP = 0.18 eV can be accounted for by the inductive effect. This correlates remarkably well with the experimental shift of the $n_\perp$ level in **1c** compared with **1a** (ΔIP = 0.16 eV). The increase of the experimental splitting for compound **1c** as compared with the reference compounds **1a** and **2b** amounts to 0.06 eV.

Since the inductive and through-bond effects are opposed for the first orbital, we can conclude that the effect of the through-bond interaction in **1c** approxinates 0.23 eV; a value equivalent to that found in the methylene system (vide-supra).

Perhydro Naphthalene Derivatives

An effective through-bond coupling requires a nearly parallel orientation between the π-resp. n-system and the interacting sigma bonds, as Hoffmann *et al.*[21] have predicted. The C(1)-C(8a) and C(7)-C(8) bonds of the *trans* configuration have this parallel orientation in contrast to their perpendicular orientation in the *cis* compound (Fig. 1). Pasman *et al.*[6] have shown that the ultraviolet absorption spectrum of the dicyano-methylene derivative of the *trans* compound shows a sigma-coupled transition. The appearance of this transition can only be explained if a through-bond coupling exists, since the spatial distance between the lone pair and the π-system precludes any overlap. It seemed interesting to test if it is possible to prove this through-bond coupling over five sigma-bonds by photoelectron-spectroscopy. A comparison of the *trans*- and *cis*-systems, **4a** and **4b** is very useful for this purpose, since any inductive effect is equal. The splitting between the IP (adiabatic) of the sulfur $n_\perp$ system and the π level in the *trans*-isomer amounts to 0.78 eV and to the *cis*-isomer 0.73 eV.

This result supports the conclusion of Pasman *et al.* from the ultraviolet-absorption spectra of the dicyano

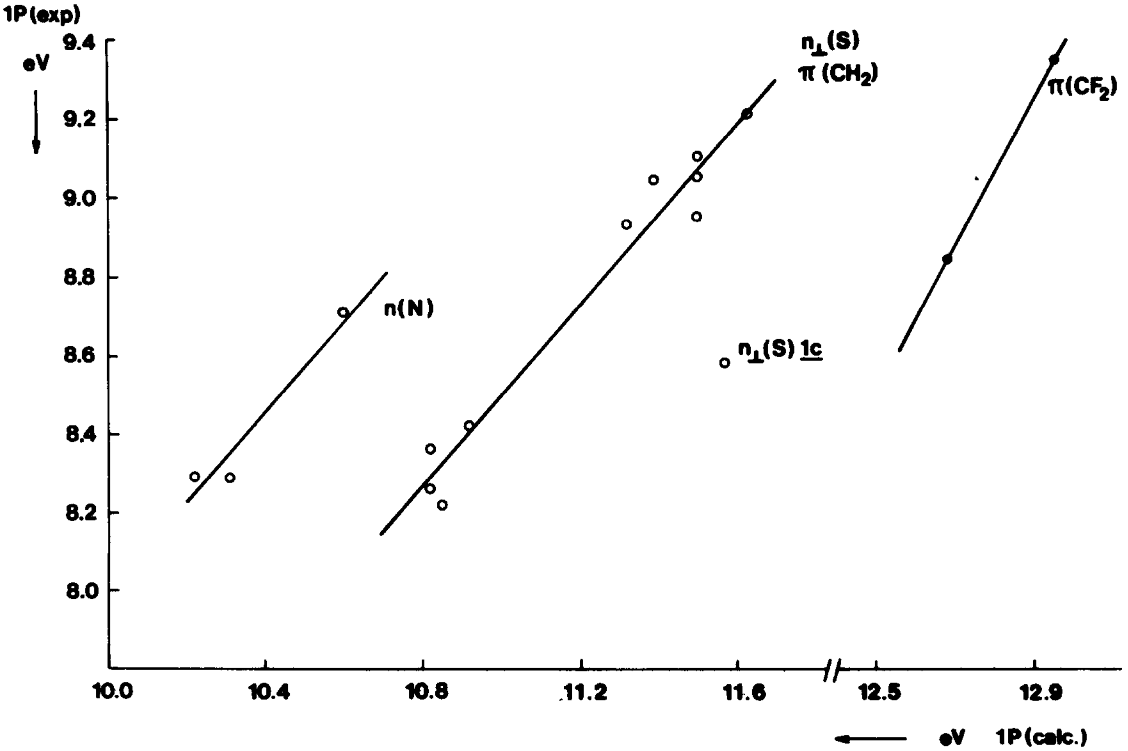

Fig. 8. MIEHM-calculated energies versus experimental IP's.

methylene derivatives. The results supports furthermore the conformational requirements for long range through bond interaction as predicted by Hoffmann *et al.*[21] and others.[22] Despite the fact that the increase of the splitting of 0.05 eV is significant we have to conclude that the observation of a sigma-coupled transition in the absorption spectra consistiutes a more sensitive tool for the detection of a long range through-bond coupling between non-equivalent groups than photoelectron spectroscopy.

EXPERIMENTAL

Analytical samples of all compounds were obtained by preparative GLC on an OV-101 column (length 3m 07 mm, 25%, V = 60 ml/min) unless otherwise stated.

Compounds **1b**, **2a**, **3b** and **4b** were prepared from the corresponding ketones following the procedure of Maercker[23] for the preparation of methylene-cyclohexane **1b**.

Compounds **1c** and **2c** were prepared from the corresponding ketones following the procedure of Fuqua[24] for the preparation of difluoromethylenecyclohexane (**1c**). Pentamethylenesulphid3 (**1a**) was a commercial product obtained from 'Aldrich' N-methyl-piperidine (**3a**) and *N*-methyl-piperidone-4 (**3d**) were obtained from 'Fluka'.

The preparation of *cis* and *trans*-6-thia-perhydronaphthalene-2-one is described elsewhere.[6]

4-*methylene-thia-cyclohexane* (**1b**)
IR($CHCl_3$): 1645 cm^{-1}: C=C; NMR (CCl_4): 4.63 (2H, s); GLC: T 120°; R_t 5.5 min.

4-*difluoromethylene-thia-cyclohexane* (**1c**)
IR($CHCl_3$): 1755 cm^{-1}: C=C; GLC: T 135°: R_t 9.3 min.

N-methyl-4-methylene-piperidine (**3b**)
IR($CHCl_3$): 1650 cm^{-1}: C=C; NMR (CCl_4): 4.61 (2H, s); GLC: T 90°: R_t 2.5 min.

Trans- and cis-2-*methylene-6-thia-perhydronaphthalene* (**4a** and **4b**). A mixture of the ketones[6] was reacted in a Wittig type reaction.[23] Work-up was accomplished by extraction with n-pentane. The resulting oil was shown to consist of starting material and products **4a** and **4b**. Therefrom **4a** and **4b** could be separated by preparative GLC on an OV-101 column (length 3m Ø7 mm, 10%, V = 60 ml/min, T 130°: $R_{t(4a)}$ 15 min, $R_{t(4b)}$ 17 min.); NMR ($CDCl_3$): 4.58 (2H, s). The photoelectron spectra were measured on a Vacuum Generator model ESCA-2 photoelectron spectrometer with a hemispherical analyser, excitation energy: 21.21 eV, resolution: 0.015 eV, accuracy 0.02 eV, argon and xenon were used for calibration.

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