ACTA CHEMICA SCANDINAVICA 22 (1968) 1655–1668

1,1′-Thiocarbonyl-bis-pyrazoles

Part I. Spectroscopic and Dipole Moment Studies

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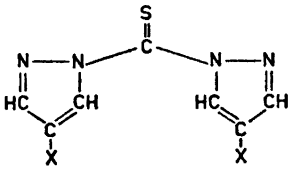
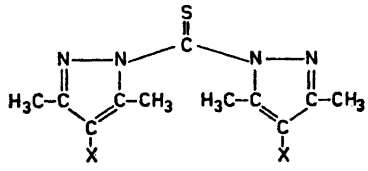
A series of 1,1′-thiocarbonyl-bis-pyrazoles, several with polar substituents in positions 3 and 4, have been prepared and their NMR and ultraviolet spectra have been recorded. The spectra have been correlated with results from molecular orbital calculations. The calculated transition energies reproduce satisfactorily the gross effect of conjugating a thiocarbonyl group with two pyrazole rings, but not the finer substituent effects. The charge distributions, on the other hand, are in reasonable agreement with the NMR chemical shifts. The conformations of the molecules are discussed in relation to the dipole moments of four representative compounds.

In a current investigation of electronic spectra and electronic structures of thioamides,[1] a simple molecular orbital method of modified ω-type [2] has been of considerable value for a semiquantitative interpretation of the physical properties of the molecules under study. We have now extended this investigation to a series of thioamides in which the nitrogen atom is part of a heteroaromatic ring, in order to test the applicability of the calculation method to larger systems, in which conjugation effects in different directions are at work.

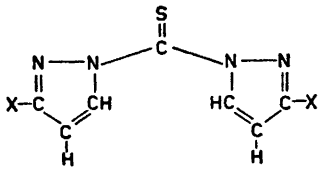
Some 1-thioacylpyrazoles have been described earlier. Scott [3] has studied 1-thiocarbamoylpyrazoles, and Ried and Beck [4] 1,1′-thiocarbonyl-bis-3,5-dimethylpyrazole (IIa). The present investigation is concerned with a number of 1,1′-thiocarbonyl-bis-pyrazoles. These can be divided into three groups: (I) with substituents only in position 4 of the pyrazole ring; (II) with methyl groups in positions 3 and 5 and with or without substituents in position 4; and (III) with substituents only in position 3. For spectral comparison, a 1-(*N*,*N*-dimethylthiocarbamoyl)-pyrazole (IV) has also been prepared.



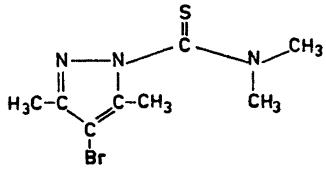
I a, X = H
b, X = Cl
c, X = Br
d, X = I
e, X = NO_2



II a, X = H
b, X = CH_3
c, X = Cl
d, X = Br
e, X = I
f, X = $CO_2C_2H_5$
g, X = NO_2



III a, X = $CO_2C_2H_5$
b, X = Ph
c, X = 2′-thienyl



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MOLECULAR ORBITAL CALCULATIONS

The Coulomb and resonance integrals used are found in Table 1. The calculations were performed with $\omega=1.0$. π-Electron and transition energies

Table 1. Coulomb and resonance integrals.

Atom	h_x[a]	Bond	k_{xy}[b]
C	0	C—C	0.8
Ṅ	0.5	C—N	0.7
N̈	1.5	C—S	0.4
N (in NO_2)	2.0	C—Cl	0.4
Ṡ	0.5	C—Br	0.3
Cl	2.0	C—I	0.2
Br	1.5	C—O	0.7
I	1.0	N—N	0.6
Ȯ	1.0	N—O	0.7
Ö	2.5		
O (in NO_2)	1.0		

[a] in $\alpha_x=\alpha_c+h_x\beta_{cc}$.
[b] in $\beta_{xy}=k_{xy}\beta_{cc}$.

Table 2. Orbital and transitions energies in units of β.

Compound	HOMO	LFMO	NBO	$\Delta E_{\pi\rightarrow\pi^*}$	$\Delta E_{n\rightarrow\pi^*}$
I a	0.469	−0.462	0.160	−0.931	−0.622
I b	0.462	−0.467	0.157	−0.929	−0.624
I c	0.464	−0.465	0.158	−0.929	−0.623
I d	0.465	−0.464	0.158	−0.929	−0.622
I e	0.505	+0.004	0.193	−0.501	−0.189
II f	0.485	−0.378	0.175	−0.863	−0.553
III	0.490	−0.272	0.182	−0.762	−0.454
IV	0.382	−0.582	0.098	−0.964	−0.670
Thiourea	0.303	−0.787	0.039	−1.090	−0.826

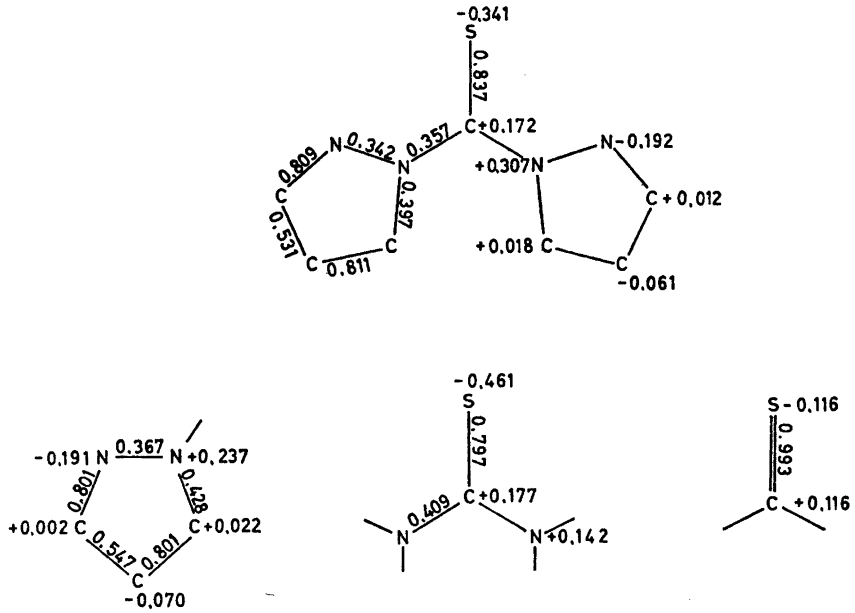

Fig. 1. π-Electron distributions and π-bond orders.

are found in Table 2, and bond orders and charge distributions for (Ia), pyrazole, thiourea and a thiocarbonyl group (same parameters) are shown in Fig. 1. Because of limited computer capacity no calculations were performed on (IIIb) and (IIIc).

NMR SPECTRA AND π-ELECTRON DENSITIES

The NMR spectrum of (Ia) consists of three quartets with τ=2.36, 2.95, and 4.31, respectively. The coupling constant between the first and the second

group is 0.7 cps, between the second and third 1.4 cps, and between the first and third 2.9 cps. Investigations on 1-acyl-[5-6] and 1-carbamoylpyrazoles [7] have given J_{34}=1.3—1.6 cps, J_{45}=2.5—3.0 cps, and J_{35}=0.6—0.7 cps. Using these constants, the three quartets in the spectrum of (Ia) can safely be assigned to the protons in position 5, 3, and 4, respectively. The high field resonance of the proton in position 4 is in agreement with the generally held view that the electron density is highest in this position (*cf.*, *e.g.*, Ref. 8). In agreement with the assigned structures, the compounds of type (I) have two doublets with a splitting of 0.7 cps, and those of type (III) two doublets with a splitting of 2.9—3.0 cps. The phenyl proton signals in (IIIb) fall in two groups, at 2.10 τ (2H) and 2.60 τ (3H). Tensmeyer and Ainsworth [6] have found that this splitting of phenyl signals requires coplanarity of the rings and is inhibited by neighboring substituents. This observation furnishes an extra proof for the structure of (IIIb). The 2′-thienyl group in (IIIc) has an AMX spectrum with H_3' at 2.45 τ, H_4' at 2.90 τ, and H_5' at 2.57 τ. J_{34} is 3.4 cps, J_{35} 1.2 cps, and J_{45} 5.1 cps.

The τ values of ring and methyl group protons in compounds (I—III) are found in Table 3. The values for the methyl protons are assumed to fall in the same order as those for the ring protons, *i.e.* the high field signal is assigned to the 3-methyl group. Since the difference between positions 3 and 5 is probably mainly determined by the magnetic anisotropy of the thiocarbonyl

Table 3. NMR spectra of 1,1′-thiocarbonyl-bis-pyrazoles I—III in 5 % solution in $CDCl_3$, and the corresponding π-electron densities.

Compound	Position					
	3		4		5	
	τ	q	τ	q	τ	q
I a	2.95r [a]	0.988	4.31r	1.061	2.36r	0.982
I b	2.16r	0.991	—	—	1.56r	0.994
I c	2.14r	0.990	—	—	1.50r	0.990
I d	2.12r	0.989	—	—	1.47r	0.987
I e	1.59r	0.975	—	—	0.84r	0.906
II a	7.77m [b]	0.988	3.87r	1.061	7.73m	0.982
II b	7.87m	0.988	8.08m	1.061	7.82m	0.982
II c	7.73m	0.991	—	—	7.67m	0.994
II d	7.70m	0.990	—	—	7.67m	0.990
II e	7.70m	0.989	—	—	7.64m	0.987
II f	7.54m	0.974	—	—	7.43m	0.921
II g	7.45m	0.975	—	—	7.18m	0.906
III a	—	—	2.99r	—	1.53r	—
III b	—	—	3.17r	—	1.45r	—
III c	—	—	3.22r	—	1.40r	—

[a] r=ring hydrogen.
[b] m=methyl hydrogen.

group, the arbitrariness of this assumption is probably not very serious. It is generally recognized that proton resonance shifts in conjugated systems are highly dependent on the π-electron charges of the atoms to which the protons are bonded. Therefore, the τ values for the ring and methyl protons of the compounds (I) and (II) have been correlated with the π-electron densities of the corresponding ring carbon atoms. A rough correspondence can be observed, as is illustrated by Fig. 2. Least squares calculations gave regression lines with slopes of 21 ppm/electron for the ring protons and 5.4 ppm/electron for the methyl protons. The first value is rather much higher than those obtained in previous investigations. By correlation of chemical shifts with HMO charge distributions for aromatic compounds Dailey *et al.*[9] found a slope of 8.0 ppm/electron, and Fraenkel *et al.*[10] and Schaefer and Schneider[11] obtained values close to 10 ppm/electron from the chemical shifts of the symmetrical species $C_5H_5^-$, C_6H_6 and $C_7H_7^+$. The small differences in ring current due to differences in ring size were also taken into account. The low value given in Ref. 9 may be due to the exaggeration of charge separations inherent in the HMO method, but the value from the ions has no such defects. The high slope

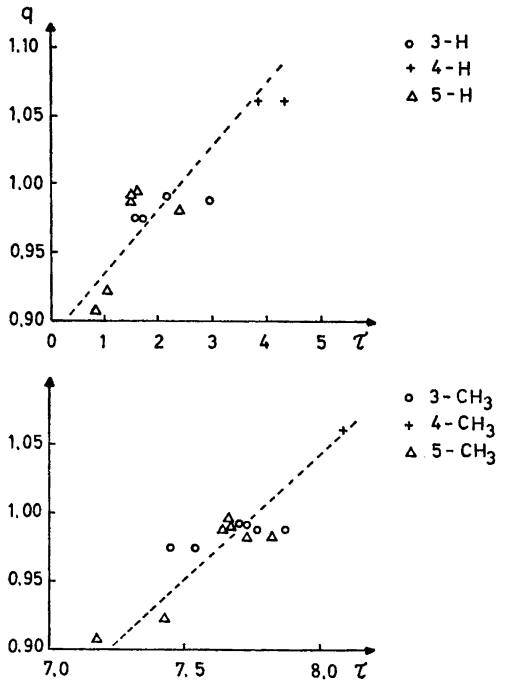

Fig. 2. Correlations of chemical shifts with calculated π-electron densities for ring protons (top) and methyl protons (bottom).

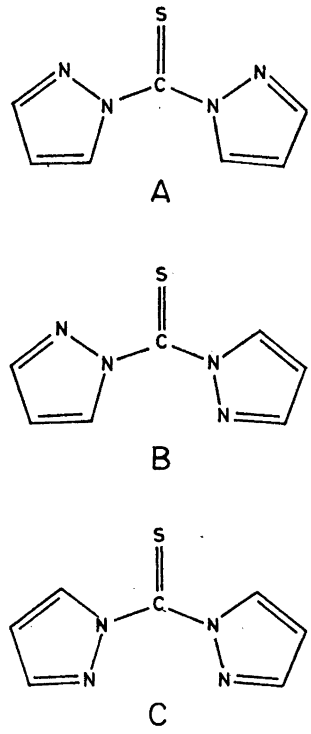

Fig. 3. Possible conformations of thiocarbonyl-bis-pyrazoles.

observed for the ring protons of (I) may be due to other effects. Inductive and anisotropy effects of the substituents, which work in the same direction as the charge distribution but which are not taken into account by the calculations, are probably the most important ones. Anisotropy of the ring nitrogen atoms and ring current should be the same for the corresponding positions in all compounds, at least as a first approximation. On the other hand, the difference between positions 3 and 5 is governed by anisotropy effects as well as by the π-electron distribution.

DIPOLE MOMENTS AND CONFORMATIONS

Assuming coplanarity of the conjugated system, the thiocarbonyl-bispyrazoles can exist in three different conformations (A—C, Fig. 3), and an attempt has been made to estimate their relative importance by a study of the dipole moments of some suitable representatives. The moments for (Ia), (Ib), (IIa), and (IIc) have been measured in benzene solution (Table 4). The moments of the conformations A—C have been estimated by vector addition. Several determinations of the dipole moments of pyrazole and 1-methylpyrazole have been reported. For pyrazole the values 2.19 D [12] and 2.33 D [13] have been obtained in dioxane, whereas lower and strongly concentration dependent values were obtained in benzene. This latter effect is ascribed to the formation of hydrogen bonded complexes with lower moments. Quite recently Kirchhoff [14] has measured the dipole moment of pyrazole in the gaseous state by the microwave technique, and his value, 2.21 ± 0.01 D, shows that association with dioxane molecules does not significantly change the dipole moment of pyrazole. The moment of 1-methylpyrazole is rather similar, and values of 2.3 D [15] and 2.28 D [16] have been reported. Unfortunately, the direction of the dipole moment in the pyrazole ring is not yet known with certainty. Orgel *et al.*,[8] using the HMO method, calculated a moment of 2.0 D for 1-methyl-

Table 4. Experimental and calculated dipole moments.

Compound	$\mu_{expt.}$D	Conformation	X	M_1 D	M_2 D	μ_π, calc. D
		A	H	3.89	5.79	3.51
I a	3.19					
		B	H	1.95	3.23	—
II a	3.37					
		C	H	2.28	0.38	0.62
		A	Cl	0.97	2.87	3.90
I b	1.96					
		B	Cl	0.97	1.64	—
II c	1.98					
		C	Cl	1.95	0.05	0.72

M_1 = sum of group moments only.
M_2 = sum of group moments and estimated mesomeric moment.

pyrazole, directed from N_1 towards N_2 and nearly parallel with the N—N bond. Using a vector addition method, with the vector components equal to the moments of pyrrole and pyridine, Giller *et al.*[13] arrived at nearly the same conclusion. Therefore, it seems reasonable to use a group moment of 2.2 D for the pyrazole ring, directed along the N_1—N_2 bond. For an unconjugated thiocarbonyl group, a bond moment can be evaluated from the dipole moment of thiofenchone, which according to Lüttringhaus and Grohmann [17] is 2.54 D, and according to Lumbroso and Andrieu [18] 2.59 D. These values give a C=S bond moment in the range 1.9—2.1 D, and the higher value is applied here for the first approximation. For the C—Cl bond a moment of 1.2 D is taken from the value for chlorobenzene,[19] and for C—H the generally accepted value of 0.4 D, with the hydrogen atom at the positive end of the dipole, is used. When these bond moments are used in the vector addition, the mesomeric interaction between the thiocarbonyl group and the pyrazole rings is neglected, and the mesomeric moment of the C—Cl bond is assumed to be the same as in chlorobenzene. The latter approximation is probably not very serious, but the thioamide mesomerism requires some consideration. The charge distribution in Fig. 1 shows that the main effect of the interaction is to increase the negative charge on the sulphur atom and to increase the positive charge on the thiocarbonyl carbon atom and on the nitrogen atoms in position 1 of the pyrazole rings. An appreciation of the importance of this effect can be obtained by allowing an interaction, which results in an increase of the negative charge of the sulphur atom by 0.15 electron and a decrease on the thiocarbonyl carbon atom and the pyrazole N_1 atoms by 0.05 electron each. This results in an extra mesomeric moment of 1.90 D, directed along the C—S bond.

The calculations have been performed with an idealized geometry, assuming the thiocarbonyl carbon atom to be exactly trigonal and the pyrazole rings to be regular pentagons. The vector sums of the simple group moments (M_1) and the sums after addition of the extra mesomeric moment (M_2) are found in Table 4. There are also found the calculated π moments for the conformations A and C.

M_2 should be the most realistic of the theoretical dipole moments in Table 4. A comparison with the experimental moments then gives the highest weight to conformation B both when X is H and Cl. This assignment gets some support from an examination of molecular models, which shows that the two methyl groups in position 5 of (II) on conformation A will overlap to such an extent that coplanarity of the two rings becomes impossible. In conformation B, on the other hand, a methyl group will be opposed to a lone pair. Theoretical [20] as well as experimental results [21] show that a lone pair in ammonia and amines is "smaller" than a hydrogen atom, at least at close approach. In pyrazole the lone pair has more *s* character and will be still more contracted. Even if some interaction may remain, this conformation can come much closer to coplanarity than A. In conformation C complete coplanarity is possible, but the existence of a large proportion of this form is ruled out by the large difference between calculated and experimental dipole moments.

The NMR spectrum of (Ia) has been recorded down to −60°C, but only the spectrum of one conformer could be observed, and no change ascribable

to slow rotation around the C—N bonds appeared. This is in harmony with the existence of one highly preferred conformation, but an equally good explanation is a low barrier to rotation. In tetramethylthiourea the rotation seems to be rapid at −60°C,[22] and in this compound the mesomeric interaction between the nitrogen atoms and the thiocarbonyl group should be stronger and consequently the barrier higher than in the compounds now under study.

ULTRAVIOLET SPECTRA

The thiocarbonyl-bis-pyrazoles are yellow to orange, and the colour is due to a low-intensity band in the region 440—480 nm. All compounds also display a high-intensity band around 300 nm, in some cases with a shoulder. The positions and intensities of the absorption bands are recorded in Table 5.

Table 5. Ultraviolet-visible spectra of compounds I—IV.

Compound	Solvent	$n\rightarrow\pi^*$		$\pi\rightarrow\pi^*$			
		λ_{max} nm	ε	λ_{max} nm	ε	λ_{max} nm	ε
I a	Ethanol	444	230	305	16 600	287(s)	13 800
	Heptane	446	220	305(s)	14 600	285	18 400
II a	Ethanol	450	360	311	16 100	—	—
	Heptane	449	410	312	21 300	—	—
II b	Ethanol	445	390	320	20 700	—	—
	Heptane	444	550	317	23 500	—	—
I b	Ethanol	447	250	308	16 000	—	—
	Heptane	447	220	308	16 700	—	—
II c	Ethanol	452	460	319	20 300	—	—
	Heptane	450	520	319	23 900	—	—
I c	Ethanol	447	240	319	12 300	—	—
	Heptane	447	280	312	20 400	—	—
II d	Ethanol	453	420	322	21 100	—	—
	Heptane	452	520	322	24 800	—	—
I d	Ethanol	447	280	327	15 200	—	—
	Heptane	450	260	323	21 100	—	—
II e	Ethanol	454	390	331	19 800	—	—
	Heptane	453	540	329	22 800	—	—
I e [a]	Heptane	470	230	290	23 800	250	20 200
II g	Ethanol	477	250	308	23 100	—	—
	Heptane	475	360	314	26 200	260	13 900
II f	Ethanol	468	330	313	22 500	220	16 300
	Heptane	466	331	315	23 800	—	—
III a	Ethanol	461	250	315(s)	11 400	290	19 000
	Heptane	456	250	312(s)	14 100	293	19 400
III b	Ethanol	442	620	340	31 300	239	16 800
	Heptane	445	600	338	36 000	239	22 300
III c	Ethanol	459(s)	1000	361	36 100	265	18 000
	Heptane	441	860	359	35 300	269	19 700
IV	Ethanol	360	300	278	10 600	—	—
	Heptane	368	380	278	12 900	—	—

[a] Decomposes in ethanol.

The low intensity band is most likely due to a $n\rightarrow\pi^*$ transition, caused by excitation of a lone pair electron on the sulphur atom to the lowest antibonding π orbital (LFMO). In most thiocarbonyl compounds the $n\rightarrow\pi^*$ band can be recognized by substantial blue-shifts with increasing solvent polarity.[23,24] In the present case, the solvent effect is very small and not always in the expected direction. A similar anomaly was observed in the spectra of some *N*-acetylthioamides,[25] and it was then ascribed to a preferential solvation at the carbonyl oxygen atom. The same explanation is feasible here. Hydrogen bonding of ethanol molecules can be expected to occur at the pyridine-type nitrogen atoms in the pyrazole rings rather than at the sulphur atom, which is probably less basic. It is of interest to note that the 1-thiocarbamoylpyrazole (IV) shows a normal solvent dependence. This may be due to a stronger polarization of the thiocarbonyl group with consequent higher basicity of the sulphur atom, since here the full conjugating power of one nitrogen atom is available.

The $n\rightarrow\pi^*$ band is fairly insensitive to weakly conjugating substituents, such as the halogens, in position 4, and also to thienyl and phenyl group in position 3, whereas carbethoxy and nitro groups cause considerable bathochromic shifts. It is worth noticing, however, that the effect of the halogens in position 4 increases in the order Cl<Br<I, which is in the order of increasing polarizability but opposed to the order of increasing +M effect.[26] The 1-thiocarbamoylpyrazole (IV) has its $n\rightarrow\pi^*$ band at considerably shorter wavelengths.

The high intensity band is ascribed to the lowest $\pi\rightarrow\pi^*$ transition. The effects of substituents on this band are rather different from what was observed for the $n\rightarrow\pi^*$ band. The largest bathochromic shifts are caused by phenyl and 2-thienyl groups in position 3. Halogen atoms in position 4 cause somewhat smaller but still substantial red shifts, also here increasing in the series Cl, Br, I. Substituents with −M effect generally give only small shifts. In the series (I) the nitro group even causes a hypsochromic shift. A similar effect is found in 1-acetylpyrazoles, where the bathochromic shift caused by the 4-nitro group is much smaller than that for other substituents.[27] Schubert *et al.*[28] have investigated the spectral effect of conjugating two −M substituents in the *p*-position of a benzene ring and find that introduction of a second nitro group in nitrobenzene assists the first $\pi\rightarrow\pi^*$ transition. This is also true for the change 4-nitropyrazole → (Ie), since 4-nitropyrazole has λ_{max}: 269 nm. In 1-acetyl-4-nitropyrazole the combination of two −M substituents has a hypsochromic effect, since this compound has λ_{max}: 260 nm. The thiocarbamoylpyrazole (IV) has its $\pi\rightarrow\pi^*$ band at considerably shorter wavelength than the thiocarbonyl-bis-pyrazoles.

The positions of the absorption maxima have been correlated with the calculated $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transition energies (Table 2). As before [29,1] the energy of the lone pair (NBO) has been equated with the Coulomb integral of sulphur in the last iteration. The compounds (I)−(IV) can be regarded as modified thioureas and therefore it seems reasonable to start the correlations from this compound. Unfortunately, its $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ bands overlap, and so do the bands of its simple alkyl derivatives. In tetramethylthiourea the bands are well separated and fall at 330 nm and 262 nm, respectively, in

Table 6. $\Delta E_I/\Delta E_X$ (experimental values from hydrocarbon solution).

Transition \ X	I a	I b	I c	I d	I e	II f	III a	IV
$n\rightarrow\pi^*$ Theor.	1.328	1.324	1.326	1.328	4.370	1.494	1.819	1.233
$n\rightarrow\pi^*$ Expt.	1.538	1.541	1.541	1.552	1.621	1.607	1.572	1.269
$\pi\rightarrow\pi^*$ Theor.	1.170	1.173	1.173	1.173	2.175	1.262	1.430	1.130
$\pi\rightarrow\pi^*$ Expt.	1.220	1.232	1.248	1.292	1.160	1.260	1.248	1.112

hydrocarbon solution.[23] Unfortunately, this compound is not suited to represent the thiourea system, since a steric effect keeps it from a planar conformation.[23] Better values for the planar system are probably around 290 nm for the $n\rightarrow\pi^*$ band and 250 nm for the $\pi\rightarrow\pi^*$ band. These wavelengths are in harmony with the transition energies calculated by Janssen.[29,30]

The building in of first one and then the other nitrogen atom of thiourea in pyrazole rings results in successive bathochromic shifts of both $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ bands. This is qualitatively reproduced by the corresponding calculated transition energies. The degree of quantitative agreement is shown in Table 6, where the experimental and calculated ratios between the transition energies of thiourea (ΔE_I) and its conjugated derivatives (ΔE_X) are shown. For the simple derivatives (IV) and (I, a—d) the agreement is not discouraging. It is worth noting, however, that the theoretical ratios are generally smaller than the experimental ones, *i.e.* that the calculations underestimate the effect of conjugation. This is rather unusual but may be ascribed to the fact that the parameters of Table 1 have been adjusted to give realistic charge distributions [2] but have not been used to correlate π-electron energies. With higher k values a better agreement might be obtained, but such a procedure would be of little real value. The larger conjugating effect of the carbethoxy and nitro groups, particularly on the $n\rightarrow\pi^*$ transitions, is reproduced, but the effect of the nitro group is vastly exaggerated. An inspection of the energy levels of both (Ie) and 4-nitropyrazole shows that the LFMO comes out with binding energy. The same absurd result is obtained with the HMO technique. This is surprising, since parameters of the same general type have been proposed by Streitwieser [31] and are widely used. Thus Güsten and Klasinc,[32] using the HMO method with a similar set, obtained an excellent correlation between π-electron densities and τ values for a series of p-substituted stilbenes. Owen [33] has made a systematic survey of the treatment of nitro compounds by the HMO method, and he has elaborated a parameter set, which gives good bond lengths and dipole moments for a variety of both C-, O-, and N-nitro compounds. It differs from the present set mainly by a very low resonance integral for the C—N bond and also by a comparatively low one for the N—O. These parameters should decrease the tendency of the nitro group to conjugate with electron donating groups, but no correlation with spectroscopic quantities has been undertaken. Calculations on 4-nitropyrazole and its 1-

Table 7.

Compound	Formula	Method	Yield %	M.p. °C	C		H		Halogen		N		S		Ref.[a]
					calc.	found	calc.	found	calc.	found	calc.	found	calc.	found	
I a	$C_7H_6N_4S$	B	70	49– 50	47.2	47.6	3.39	3.64	—	—	31.4	31.1	18.0	18.1	34
I b	$C_7H_4Cl_2N_4S$	B	60	123–124	34.0	34.6	1.63	1.42	28.7	28.3	22.7	22.8	13.0	13.0	35
I c	$C_7H_4Br_2N_4S$	B	61	128–129	25.0	25.0	1.20	1.12	47.6	47.9	16.7	16.7	9.54	9.49	36
I d	$C_7H_4I_2N_4S$	B	72	121–122	19.6	19.8	0.94	1.01	59.0	58.9	13.0	13.0	7.46	7.60	37
I e	$C_7H_4N_6O_4S$	B	45	108–109	31.1	31.5	1.50	1.57	—	—	31.3	31.6	12.0	11.8	38
II a	$C_{11}H_{14}N_4S$	A	76	117–118[b]	—	—	—	—	—	—	—	—	—	—	39
II b	$C_{13}H_{18}N_4S$	A	82	117–118	59.5	59.5	6.91	6.87	—	—	21.4	21.3	12.2	12.1	40
II c	$C_{11}H_{12}Cl_2N_4S$	B	47	101–102	43.6	43.6	3.99	4.01	23.4	23.4	18.5	18.5	10.6	10.6	41
II d	$C_{11}H_{12}Br_2N_4S$	B	64	105–106	33.7	33.5	3.09	3.06	40.8	40.7	14.3	14.3	8.16	8.20	42
II e	$C_{11}H_{12}I_2N_4S$	B	71	184–185	27.2	27.3	2.50	2.77	52.2	52.9	11.5	11.5	6.60	6.80	43
II f	$C_{17}H_{22}N_4O_4S$	B	71	80– 81	54.0	54.0	5.86	5.98	—	—	14.8	14.8	8.47	8.36	44
II g	$C_{11}H_{12}N_6O_4S$	B	42	157–158	40.7	40.9	3.73	3.77	—	—	25.9	25.7	9.88	9.90	45
III a	$C_{13}H_{14}N_4O_4S$	B	65	88– 89	48.4	48.6	4.38	4.29	—	—	17.4	17.5	9.95	9.92	46
III b	$C_{19}H_{14}N_4S$	B	76	171–172	69.1	69.4	4.27	4.36	—	—	17.0	17.2	9.70	9.80	47
III c	$C_{15}H_{10}N_4S_3$	B	75	156–157	52.6	52.9	2.94	2.85	—	—	16.4	16.6	28.1	27.9	48
IV	$C_8H_{12}BrN_3S$	B	88	88– 89	36.7	36.6	4.62	4.40	30.5	31.4	16.0	15.9	12.2	12.0	42

[a] Refers to preparation of pyrazole.
[b] Lit.[4] 114°.

thiocarbonyl derivative with a set of parameters adjusted according to these principles, gave even worse agreement than the previous set. Clearly, the representation of orbital energies of nitro compounds by the HMO method merits some attention.

EXPERIMENTAL

Preparative part

The pyrazoles used as starting materials were prepared by known methods. References are given in Table 7. The thiocarbonylpyrazoles were prepared by either of two methods. Method A was used by Ried and Beck [4] and is performed by refluxing thiophosgene with four molar proportions of the appropriate pyrazole in dry acetone. Half the quantity of the pyrazole is deposited as hydrochloride, and the desired product is obtained on working up the solution. In Method B thiophosgene is refluxed with two molar proportions of the pyrazole in dry benzene. Hydrogen chloride is evolved and ultimately a complete conversion is achieved. This method works best with the least basic pyrazoles such as the 4-nitro- and 4-carbethoxy derivatives, and it requires rather long reflux times with the more basic ones. Purification of the crude products could mostly be achieved by recrystallization from heptane or benzene-heptane and similar solvent mixtures, but in one case (Ia) column chromatography on silica was necessary. The compound (IV) was prepared by refluxing 3,5-dimethyl-4-bromopyrazole with one molar proportion of dimethylthiocarbamoyl chloride in benzene.

The preparative and analytical results are summarized in Table 7.

Dipole moment measurements

These were performed with a Dipolmeter, Type DM 01, from Wissenschaftlich-Technischen Werkstätten GmbH in a cell of 25 ml volume. The meter settings were calibrated with the aid of benzene and dibutyl ether purified according to the directions in the instrument manual. The measurements were performed in benzene solution with the weight fractions in the range 0.006–0.06. Indices of refraction of the solutions were determined with a Carl Zeiss type Abbe refractometer. The dipole moments were evaluated by the method introduced by Smith [49] and Guggenheim.[50] The slopes of the straight lines representing $\varepsilon_{12}-\varepsilon_1$ and $n_{12}^2-n_1^2$ *versus* weight fraction of solute, k_1 and k_2, were obtained by the method of least squares. The results are found in Table 8.

Table 8.

Compound	$k_1 \times 10^{-2}$	Correlation coefficient	$k_2 \times 10^{-2}$	Correlation coefficient
I a	6.9573	0.9999	0.5710	0.9981
I b	2.1263	1.0000	0.3815	0.9987
II a	5.8645	0.9998	0.4326	0.9997
II c	1.8883	1.0000	0.4429	0.9978

The ultraviolet absorption spectra were recorded with a Cary Model 15 spectrophotometer, and *the numerical calculations* were performed with the electronic digital computer SMIL of the Department of Numerical analysis of the Univeristy of Lund.

Acknowledgements. We are grateful to the *Swedish Natural Sciences Research Council* for a grant which made possible the purchase of a Cary Model 15 recording spectrometer and also for a general research grant, to Fil.Mag. Kerstin Malmqvist and Fil.Kand. Leif Robertsson for programming the computer calculations, and to Fil.Kand. Sven Liljefors for a gift of a sample of 3-[2-thienyl]-pyrazole.

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Received January 4, 1968.