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## Charge-Transfer Complexes of Hydrazones. VI.\* Structures of Six Hydrazone Derivatives. Infrared and Structural Evidence for Substituent Effects on Charge-Transfer Interactions

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### Abstract

The problems connected with the formation of charge-transfer complexes were examined by analysis of the IR spectra of 21 phenylhydrazones and determination of the crystal structures of six of them at room temperature with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Benzaldehyde methyl(phenyl)hydrazone (compound 2): C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>,  $M_r = 210.3$ , monoclinic,  $P2_1/a$ ,  $a = 22.896 (2)$ ,  $b = 9.201 (2)$ ,  $c = 5.559 (2) \text{ \AA}$ ,  $\beta = 91.53 (3)^\circ$ ,  $V = 1170.7 (5) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.19 \text{ g cm}^{-3}$ ,  $\mu = 5.19 \text{ cm}^{-1}$ ,  $F(000) = 448$ , the final  $R$  was 0.055 for 709 observed reflections. Acetophenone methyl(phenyl)hydrazone (compound 5): C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>,  $M_r = 224.3$ , orthorhombic,  $P2_12_12_1$ ,  $a = 20.099 (3)$ ,  $b = 8.644 (2)$ ,  $c = 7.537 (2) \text{ \AA}$ ,  $V = 1309.5 (5) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.14 \text{ g cm}^{-3}$ ,  $\mu = 4.90 \text{ cm}^{-1}$ ,  $F(000) = 480$ , the final  $R$  was 0.051 for 921 observed reflections. Benzophenone methyl(phenyl)hydrazone (compound

8): C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>,  $M_r = 286.4$ , monoclinic,  $P2_1/n$ ,  $a = 16.122 (2)$ ,  $b = 10.482 (2)$ ,  $c = 9.586 (2) \text{ \AA}$ ,  $\beta = 92.35 (3)^\circ$ ,  $V = 1618.6 (5) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.17 \text{ g cm}^{-3}$ ,  $\mu = 5.01 \text{ cm}^{-1}$ ,  $F(000) = 608$ , the final  $R$  was 0.044 for 1584 observed reflections. Benzophenone diphenylhydrazone (compound 9): C<sub>25</sub>H<sub>20</sub>N<sub>2</sub>,  $M_r = 348.4$ , monoclinic,  $P2_1/n$ ,  $a = 12.355 (2)$ ,  $b = 13.741 (3)$ ,  $c = 11.543 (2) \text{ \AA}$ ,  $\beta = 96.13 (2)^\circ$ ,  $V = 1948.5 (6) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.19 \text{ g cm}^{-3}$ ,  $\mu = 5.03 \text{ cm}^{-1}$ ,  $F(000) = 736$ , the final  $R$  was 0.043 for 2761 observed reflections. *p*-Methoxybenzaldehyde methyl(phenyl)hydrazone (compound 11): C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O,  $M_r = 240.3$ , orthorhombic,  $P2_12_12_1$ ,  $a = 25.980 (3)$ ,  $b = 9.017 (2)$ ,  $c = 5.606 (2) \text{ \AA}$ ,  $V = 1313.3 (6) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.22 \text{ g cm}^{-3}$ ,  $\mu = 5.78 \text{ cm}^{-1}$ ,  $F(000) = 512$ , the final  $R$  was 0.041 for 826 observed reflections. 2-Nitrobenzaldehyde methyl(phenyl)hydrazone (compound 12): C<sub>14</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>,  $M_r = 255.3$ , monoclinic,  $P2_1/a$ ,  $a = 18.567 (2)$ ,  $b = 8.109 (2)$ ,  $c = 8.592 (1) \text{ \AA}$ ,  $\beta = 94.09 (2)^\circ$ ,  $V = 1290.3 (4) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.31 \text{ g cm}^{-3}$ ,  $\mu = 7.04 \text{ cm}^{-1}$ ,  $F(000) = 536$ , the final  $R$

\* Part V: Bruni, Tosi & Cardellini (1988).

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Table 1.  $\lambda$  absorptions (nm) of complexes of the 21 analysed phenylhydrazones ( $R_1R_2C=N-NR_3R_4$ ) with TCNE and chloranil in benzene and dichloroethane.

	$R_1$	$R_2$	$R_3$	$R_4$	TCNE		CA	
					Benzene	DCE	Benzene	DCE
1	Ph	H	Ph	H	732 (M)	728 (M)	645 (M)	637 (M)
2	Ph	H	Ph	CH <sub>3</sub>	797 (S)	797 (S)	682 (M)	698 (M)
3	Ph	H	Ph	Ph	781 (W)	781 (W)	667 (W)	679 (mW)
4	Ph	CH <sub>3</sub>	Ph	H	802 (mW)	802 (mW)	678 (mW)	650 (M)
5	Ph	CH <sub>3</sub>	Ph	CH <sub>3</sub>	No	No	No	No
6	Ph	CH <sub>3</sub>	Ph	Ph	No	No	No	No
7	Ph	Ph	Ph	H	778 (S)	773 (S)	655 (S)	655 (M)
8	Ph	Ph	Ph	CH <sub>3</sub>	No	No	No	No
9	Ph	Ph	Ph	Ph	No	No	No	No
10	<i>p</i> OCH <sub>3</sub> Ph	H	Ph	H	760 (S)	770 (S)	673 (M)	677 (M)
11	<i>p</i> OCH <sub>3</sub> Ph	H	Ph	CH <sub>3</sub>	837 (S)	848 (S)	716 (M)	723 (M)
12	<i>o</i> NO <sub>2</sub> Ph	H	Ph	CH <sub>3</sub>	No	No	No	No
13	<i>p</i> OCH <sub>3</sub> Ph	H	Ph	Ph	856 (S)	860 (M)	726 (W)	739 (M)
14	<i>p</i> NO <sub>2</sub> Ph	H	Ph	H	709 (W)	672 (W)	602 (W)	608 (W)
15	<i>p</i> NO <sub>2</sub> Ph	H	Ph	CH <sub>3</sub>	746 (M)	755 (M)	610 (W)	632 (M)
16	<i>o</i> NO <sub>2</sub> Ph	H	Ph	H	702 (M)	700 (M)	No	No
17	Ph	H	<i>o</i> NO <sub>2</sub> Ph	H	No	No	No	No
18	Ph	H	<i>p</i> NO <sub>2</sub> Ph	H	(vW)	(vW)	No	No
19	Ph	CH <sub>3</sub>	<i>o</i> NO <sub>2</sub> Ph	H	No	No	No	No
20	Ph	Ph	<i>o</i> NO <sub>2</sub> Ph	H	No	No	No	No
21	Ph	Ph	<i>p</i> NO <sub>2</sub> Ph	H	(vW)	(vW)	(vW)	No

Symbols: TCNE = tetracyanoethylene; Ph = phenyl; DCE = 1,2-dichloroethane; M = medium; mW = medium-weak; vW = very weak; W = weak; S = strong; CA = chloranil; No = no evidence of CT interaction.

was 0.069 for 709 observed reflections. In phenylhydrazones the possibility of obtaining a charge-transfer interaction is related to the absence of even a slight amount of strain in the hydrazono group, which must be perfectly planar to allow conjugation of the group. Mesomeric and inductive effects of substituents contribute only to the stability and the amount of interaction.

### Introduction

Previous studies (Marchetti & Tosi, 1972; Bruni, Cardellini & Tosi, 1981; Tosi, Bruni & Cardellini, 1983; Bocelli, Tosi & Cardellini, 1984; Bruni, Tosi & Cardellini, 1988) described the determination of thermodynamic parameters and formation constants of charge-transfer complexes (CTC) between phenylhydrazones and organic acceptors. In these papers, it was pointed out that the possibility of obtaining, in solution, a CT interaction was related to the presence of at least one H atom bonded to the atoms of the phenylhydrazone skeleton ( $>C=N-N<$ ). Table 1 reports a list of the most indicative acceptors and donors investigated so far, together with the  $\lambda_{CT}$  values in benzene and dichloroethane (and a qualitative indication of the strength of CTC obtained).

In no case was it possible to isolate a CTC in the solid state.

Because X-ray determinations do not show any interactions other than van der Waals ones and the solvents used in the formation of the CTC between our phenylhydrazones and the acceptors, mainly benzene

and 1,2-dichloroethane, do not influence the main absorption frequencies of phenylhydrazones, it is conceivable that these phenylhydrazones preserve almost the same conformation on going from the solid to the solution state. This situation is quite common in hindered hydrazones in which restricted rotation occurs around the N-N bond (Lunazzi & Placucci, 1977).

In this regard, X-ray determinations on compounds 2, 5, 8, 9, 11 and 12, together with IR analysis in the solid state and in solution, were undertaken in order to determine general electronic and structural parameters that may affect, in solution, the formation of the CTC.

### Experimental

#### Spectroscopy

Solid-state IR spectra were obtained using a Nicolet Fourier Transform Infrared 60 SX Spectrometer equipped with a multiple internal reflectance apparatus.

The IR determinations were performed on powdered compounds 1-21. The IR spectra of compounds 1-10, already analysed (Arnold & Schiele, 1969), were reinvestigated in order to achieve comparison of data obtained using a standardized procedure.

Solution IR spectra were recorded on a Perkin Elmer Mod. 298; UV-visible determinations were obtained, at 298 K, with a Perkin Elmer Mod. 554 spectrophotometer equipped with an MgW-K2R thermostating system for circulating water. Compounds and solvents were prepared following standard methods (Vogel, 1957). Chloranil (Carlo Erba RP ACS reagent) was twice recrystallized from acetone and

Table 2. *Crystal and experimental data for compounds 2, 5, 8, 9, 11 and 12*

	(2)	(5)	(8)	(9)	(11)	(12)
Formula	C <sub>14</sub> H <sub>14</sub> N <sub>2</sub>	C <sub>15</sub> H <sub>16</sub> N <sub>2</sub>	C <sub>20</sub> H <sub>18</sub> N <sub>2</sub>	C <sub>25</sub> H <sub>20</sub> N <sub>2</sub>	C <sub>15</sub> H <sub>16</sub> N <sub>2</sub> O	C <sub>14</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub>
<i>M<sub>r</sub></i>	210.3	224.3	286.4	348.4	240.3	255.3
<i>a</i> (Å)	22.896 (3)	20.099 (3)	16.122 (2)	12.355 (2)	25.980 (3)	18.567 (2)
<i>b</i> (Å)	9.201 (2)	8.644 (2)	10.482 (2)	13.741 (3)	9.017 (2)	8.109 (2)
<i>c</i> (Å)	5.559 (2)	7.537 (2)	9.586 (2)	11.453 (2)	5.606 (2)	8.592 (1)
$\alpha$ (°)	90	90	90	90	90	90
$\beta$ (°)	91.53 (3)	90	92.35 (3)	96.13 (2)	90	94.09 (2)
$\gamma$ (°)	90	90	90	90	90	90
<i>V</i> (Å <sup>3</sup> )	1170.7 (5)	1309.5 (5)	1618.6 (5)	1948.5 (6)	1313.3 (6)	1290.3 (4)
Space group	<i>P</i> 2 <sub>1</sub> / <i>a</i> *	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i> *	<i>P</i> 2 <sub>1</sub> / <i>n</i> *	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>a</i> *
<i>D<sub>x</sub></i> (g cm <sup>-3</sup> )	1.19	1.14	1.17	1.19	1.22	1.31
<i>Z</i>	4	4	4	4	4	4
$\mu$ (cm <sup>-1</sup> )	5.19	4.90	5.01	5.03	5.78	7.04
<i>F</i> (000)	448	480	608	736	512	536
Number of collected reflections	1459	1458	2834	4033	1505	2828
Number of independent reflections	1205	1458	2536	3751	1481	2503
Number of observed reflections [ <i>I</i> ≥ 2σ( <i>I</i> )]	709	921	1584	2761	826	709
Range of <i>h, k, l</i>	0–±22, 0–9, 0–5	0–23, 0–10, 0–9	0–±17, 0–12, 0–10	0–±14, 0–16, 0–13	0–30, 0–10, 0–6	0–±20, 0–8, 0–10
Final ( $\Delta/\sigma$ ) <sub>max</sub>	0.12	0.17	0.15	0.14	0.08	0.17
Final ( $\Delta\rho$ ) <sub>max</sub> (e Å <sup>-3</sup> )	0.93	0.32	0.22	0.52	0.16	0.18
Habit of specimen	Prismatic	Pyramidal	Octahedral	Prismatic	Prismatic	Prismatic
Dimensions (mm)	0.05 × 0.06 × 0.14	0.03 × 0.04 × 0.045	0.03 × 0.03 × 0.05	0.05 × 0.07 × 0.11	0.03 × 0.06 × 0.15	0.04 × 0.07 × 0.11
Colour	Colourless	Yellow	Yellow	Yellow	Colourless	Red

\* Alternative setting of *P*2<sub>1</sub>/*c* (No. 14).

vacuum dried. Tetracyanoethylene (Aldrich pure reagent) was recrystallized three times from chlorobenzene and sublimed in vacuum at 383 K and a pressure of 0.04 kPa. Colourless crystals were obtained. All solvents were Carlo Erba RP ACS grade reagents and were dried and purified according to Vogel (1957).

### X-ray analyses

Table 2 reports cell parameters, crystal data and most experimental information for derivatives 2, 5, 8, 9, 11 and 12.

Preliminary cell parameters were obtained as part of the alignment process of the crystal on the diffractometer using the angular values of 19–26 reflections automatically well centred on the diffractometer using a routine which repeatedly improves the angular values to reach the maximum of the peak until the angles remain invariant within 0.001°. All data were measured ( $3 \leq \theta \leq 70^\circ$ ) at room temperature on a Siemens AED single-crystal diffractometer equipped with a General Automation Jumbo 220 computer using Cu *K*α radiation. The integrated intensities were obtained by a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) procedure. A standard reflection monitored every fifty measurements was stable for all the derivatives, except for compound 12, for which a decrease in intensity was observed. The data were corrected for this variation and all for Lp effects but not for absorption. Atomic scattering factors from *SHELX76* (Sheldrick, 1976).

*Compound 2*: the structure was solved by direct methods with *SHELX76* and refined on *F* by full-matrix least squares first isotropically (*R* = 0.14) and then anisotropically (*R* = 0.10). All H atoms located in a  $\Delta F$  map. The final *R* was 0.055 and *wR* = 0.059 with  $w = 0.3809/(\sigma^2 F + 0.00887 F^2)$ .

*Compound 5*: the structure was solved with *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined by full-matrix least squares with *SHELX76* using isotropic (*R* = 0.12) and then anisotropic (*R* = 0.08) temperature factors. All H atoms were found in a  $\Delta F$  map computed at this stage. In the final cycles six reflections, probably affected by extinction, were omitted. The final *R* was 0.051 and *wR* = 0.058 with  $w = 1.0/(\sigma^2 F + 0.02649 F^2)$ .

*Compound 8*: the structure was solved by direct methods with *SHELX76* and refined, first isotropically (*R* = 0.12) and then anisotropically (*R* = 0.09) by full-matrix least squares. The H atoms, located in a  $\Delta F$  map, were refined isotropically. The refinement converged to a final *R* = 0.044 and *wR* = 0.046 with  $w = 1.0/(\sigma^2 F + 0.02407 F^2)$ .

*Compound 9*: the structure was solved by direct methods with *SHELX76*, and the refinement, H atoms from  $\Delta F$  map, first isotropic (*R* = 0.13) and then anisotropic (*R* = 0.09), converged to a final *R* = 0.043 and *wR* = 0.051 with  $w = 1.0/(\sigma^2 F + 0.00170 F^2)$ .

*Compound 11*: the structure was solved with *MULTAN80* and refined by full-matrix least squares (isotropic *R* = 0.098, anisotropic *R* = 0.076). All H atoms were located in a  $\Delta F$  map. The final *R* was 0.034 and *wR* = 0.041 with  $w = 0.3504/(\sigma^2 F + 0.01154 F^2)$ .

**Compound 12:** during the data collection the check reflection showed a decrease in intensity of about 5%. The structure was solved by direct methods with *SHELX76*. The refinement was carried out by full-matrix least squares ( $R = 0.17$  isotropic,  $R = 0.10$  anisotropic). The H atoms were all located in a  $\Delta F$  map. Seven reflections were omitted in the last cycles. The final  $R$  was 0.069 and  $wR = 0.077$  with  $w = 1.7418/(\sigma^2 F + 0.00165F^2)$ .

The calculations for compound 2 were performed with the *CRYSRULER* package (Rizzoli, Sangermano, Calestani & Andreotti, 1987) on an AT IBM personal computer, while the Gould SEL 32/77 computer was employed for the remaining five compounds.

Tables 3–8 report the atomic coordinates of compounds 2, 5, 8, 9, 11 and 12 respectively. The molecules are illustrated in Figs. 1–6. Selected bond distances and angles are in Table 9.\*

### Results and discussion

A long series of phenylhydrazones has already been analysed by X-ray techniques and many of them showed intramolecular or intermolecular hydrogen bonds involving the NH group of the aliphatic chain. Moreover, of the derivatives in Table 1, the crystal structures of compounds 1 (Vickery, Willey & Drew, 1985; de Vere, 1965), 17 (Drew, Vickery & Willey, 1984) and 18 (Vickery *et al.*, 1985) were already known. In our six derivatives, the absence of the NH group nullifies the possibility of this type of hydrogen bond. Moreover, a strong intramolecular hydrogen bond exists in compound 12 between the CH group of the aliphatic chain and the O1 atom of the *ortho* nitro group:  $O1 \cdots H13 = 2.02$  (5),  $C13 \cdots O1 = 2.77$  (1) Å,  $O1 \cdots H13 - C13 = 123.9$  (32)°. The O1 atom is also involved in a weak intermolecular contact with H18:  $O1 \cdots H18^i = 2.60$  (5) Å [ $(i) = -x - \frac{1}{2}, y, -z - 1$ ]. No intermolecular hydrogen bonds involving H13 were found in compounds 2 and 12 and this fact may be ascribed to the steric constraints of the nitro and methyl groups which surround the H13 atom.

The distances involving the N atoms of the chain do not fall into the patterns established (Willey & Drew, 1983, 1985; Drew, Vickery & Willey, 1984) for phenylhydrazones with or without intramolecular hydrogen bonds. In our derivatives these bonds seem, like the bond angles, to be independent of the type of substituents on the chain and the presence of a

Table 3. Atomic fractional coordinates ( $\times 10^4$ ) and  $U_{eq}$  values ( $\text{Å}^2 \times 10^4$ ) for compound 2

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
N1	3761 (2)	526 (5)	-928 (7)	857 (20)
N2	3323 (2)	707 (5)	644 (6)	752 (18)
C1	4263 (2)	1336 (6)	-557 (8)	748 (22)
C2	4323 (3)	2264 (6)	1416 (9)	822 (24)
C3	4811 (3)	3093 (7)	1776 (10)	923 (25)
C4	5273 (3)	3072 (7)	208 (11)	968 (26)
C5	5221 (3)	2158 (8)	-1751 (12)	1030 (29)
C6	4730 (4)	1339 (9)	-2123 (13)	990 (33)
C7	3704 (4)	-576 (9)	-2898 (12)	1149 (38)
C13	2845 (2)	-32 (6)	423 (9)	750 (24)
C14	2379 (2)	194 (6)	2157 (8)	740 (20)
C15	2420 (3)	1219 (7)	4008 (10)	844 (27)
C16	1977 (3)	1343 (8)	5636 (10)	911 (28)
C17	1485 (3)	483 (7)	5434 (10)	890 (27)
C18	1437 (3)	-512 (7)	3601 (11)	932 (28)
C19	1879 (3)	-646 (7)	1998 (11)	841 (26)

Table 4. Atomic fractional coordinates ( $\times 10^4$ ) and  $U_{eq}$  values ( $\text{Å}^2 \times 10^4$ ) for compound 5

	x	y	z	$U_{eq}$
N1	3213 (2)	4512 (4)	2940 (6)	694 (13)
N2	3817 (2)	4449 (4)	3580 (6)	716 (13)
C1	2894 (2)	6009 (4)	3019 (5)	547 (11)
C2	2225 (2)	6192 (7)	2563 (6)	671 (14)
C3	1930 (3)	7657 (7)	2654 (7)	816 (19)
C4	2300 (3)	8925 (7)	3234 (9)	891 (21)
C5	2951 (3)	8749 (6)	3680 (8)	807 (18)
C6	3261 (3)	7315 (5)	3566 (7)	654 (15)
C7	2795 (3)	3115 (6)	2803 (9)	732 (19)
C13	4200 (2)	3179 (5)	3369 (5)	622 (14)
C14	4765 (2)	3131 (5)	4534 (6)	620 (13)
C15	4812 (3)	4131 (6)	6003 (7)	742 (18)
C16	5350 (3)	4045 (7)	7143 (8)	870 (21)
C17	5851 (3)	2968 (8)	6880 (8)	860 (20)
C18	5797 (3)	1983 (8)	5457 (8)	861 (20)
C19	5271 (2)	2064 (6)	4295 (7)	737 (16)
C20	4257 (4)	2446 (11)	1609 (8)	993 (27)

hydrogen bond (in compound 12). In derivative 12, the presence of the hydrogen bond markedly affects some geometrical parameters which assume values significantly different from those of the remaining derivatives:  $C14 - C13 - H13 = 113.1$  (3)°,  $H15 \cdots H6 = 2.94$  (7) Å. The *ortho* nitro group is twisted by an angle of 21.2 (2)° and this value is very large compared with those observed in other similarly substituted phenylhydrazones (range 5.4–14.4°) (Willey & Drew, 1983; Vickery, Willey & Drew, 1981). No definite trends are discernible, in our derivatives, for the correlation between the bond orders of  $C1 - N1$ ,  $N1 - N2$  and  $N2 = C13$  distances clearly found for other phenylhydrazones (Vickery *et al.*, 1981; Drew & Willey, 1985).

Least-squares-planes analyses show that the molecules, as a whole, are, as expected, not planar; the phenylhydrazone fragments too are not perfectly planar, the dihedral angle between the phenyl ring and the  $C1$ ,  $N1$ ,  $N2$  plane ranging from 3.5 (3)° (compound 2) to 21.6 (2)° (compound 9). In this last compound the pyramidal character of the  $N1$  atom (measured

\* Lists of structure factors, thermal parameters, H-atom coordinates and full lists of bond distances, bond angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44367 (78 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. Atomic fractional coordinates ( $\times 10^4$ ) and  $U_{eq}$  values ( $\text{\AA}^2 \times 10^4$ ) for compound 8

	x	y	z	$U_{eq}$
N1	1109 (1)	825 (2)	395 (2)	528 (7)
N2	1242 (1)	359 (2)	1729 (2)	493 (6)
C1	518 (1)	1824 (2)	302 (2)	486 (7)
C2	146 (2)	2182 (3)	-984 (3)	635 (9)
C3	-447 (2)	3155 (3)	-1037 (4)	790 (12)
C4	-674 (2)	3760 (3)	148 (4)	822 (12)
C5	-292 (2)	3443 (3)	1410 (3)	699 (10)
C6	302 (1)	2488 (2)	1498 (3)	576 (8)
C7	1273 (2)	62 (3)	-837 (3)	641 (11)
C13	1851 (1)	-396 (2)	2075 (2)	466 (8)
C14	1846 (1)	-877 (2)	3537 (2)	488 (7)
C15	1100 (2)	-959 (3)	4250 (3)	587 (9)
C16	1099 (2)	-1367 (3)	5606 (3)	680 (10)
C17	1840 (2)	-1706 (3)	6323 (3)	672 (10)
C18	2578 (2)	-1621 (3)	5636 (3)	646 (9)
C19	2586 (1)	-1221 (2)	4257 (2)	533 (8)
C20	2574 (1)	-760 (2)	1216 (2)	506 (7)
C21	3098 (2)	174 (3)	736 (3)	637 (9)
C22	3770 (2)	-142 (3)	-47 (3)	802 (12)
C23	3915 (2)	-1407 (4)	-381 (3)	833 (13)
C24	3406 (2)	-2343 (3)	92 (3)	742 (10)
C25	2741 (2)	-2034 (2)	904 (3)	613 (9)

Table 6. Atomic fractional coordinates ( $\times 10^4$ ) and  $U_{eq}$  values ( $\text{\AA}^2 \times 10^4$ ) for compound 9

	x	y	z	$U_{eq}$
N1	2365 (1)	3259 (1)	9068 (1)	546 (5)
N2	3357 (1)	2893 (1)	8824 (1)	506 (5)
C1	2423 (1)	4232 (1)	9521 (1)	468 (5)
C2	1491 (2)	4814 (1)	9463 (2)	541 (6)
C3	1550 (2)	5753 (1)	9920 (2)	667 (7)
C4	2525 (2)	6119 (2)	10443 (2)	742 (8)
C5	3453 (2)	5540 (1)	10507 (2)	691 (7)
C6	3406 (1)	4598 (1)	10063 (2)	551 (6)
C7	1382 (1)	2954 (1)	8357 (1)	491 (6)
C8	503 (1)	2587 (1)	8890 (2)	581 (7)
C9	-437 (2)	2293 (1)	8220 (2)	696 (7)
C10	-498 (2)	2363 (2)	7015 (2)	751 (9)
C11	351 (2)	2729 (2)	6488 (2)	766 (9)
C12	1308 (2)	3031 (1)	7160 (2)	628 (7)
C13	3433 (1)	1965 (1)	8577 (1)	461 (5)
C14	4481 (1)	1655 (1)	8178 (1)	485 (5)
C15	5144 (1)	2323 (1)	7690 (2)	574 (6)
C16	6129 (2)	2029 (2)	7313 (2)	692 (7)
C17	6444 (2)	1063 (2)	7397 (2)	712 (7)
C18	5786 (2)	399 (1)	7865 (2)	723 (7)
C19	4810 (1)	687 (1)	8267 (2)	622 (6)
C20	2630 (1)	1208 (1)	8814 (2)	503 (5)
C21	2458 (2)	997 (2)	9955 (2)	678 (7)
C22	1732 (2)	261 (2)	10180 (2)	838 (9)
C23	1186 (2)	-257 (2)	9277 (3)	803 (9)
C24	1352 (2)	-44 (1)	8138 (2)	717 (8)
C25	2083 (1)	683 (1)	7905 (2)	584 (6)

as the out of plane distance with respect to its three bonded atoms) shows the greatest value of 0.24 (1)  $\text{\AA}$  vs a minimum of 0.02 (1)  $\text{\AA}$  for compound 2. The angles formed by some planar parts of the molecules are in Table 10.

Table 11 reports the most characteristic absorptions in the solid state and in solution in different solvents of all investigated phenylhydrazones.\* The main indica-

\* A complete band assignment of compounds 1-10 is available from one of the authors (GT) on request.

Table 7. Atomic fractional coordinates ( $\times 10^4$ ) and  $U_{eq}$  values ( $\text{\AA}^2 \times 10^4$ ) for compound 11

	x	y	z	$U_{eq}$
O1	-1208 (1)	133 (3)	1072 (6)	854 (11)
N1	1278 (1)	72 (4)	8737 (7)	762 (12)
N2	877 (1)	240 (3)	7164 (7)	693 (11)
C1	1705 (1)	1015 (4)	8411 (7)	637 (12)
C2	2114 (2)	1022 (6)	9973 (9)	890 (18)
C3	2516 (2)	1984 (7)	9694 (11)	992 (20)
C4	2536 (2)	2949 (5)	7819 (9)	813 (17)
C5	2132 (2)	2939 (5)	6232 (10)	801 (16)
C6	1721 (2)	1988 (5)	6459 (9)	737 (16)
C7	1242 (3)	-921 (7)	10753 (11)	919 (23)
C13	466 (2)	-496 (4)	7363 (8)	673 (14)
C14	42 (1)	-306 (4)	5708 (8)	649 (14)
C15	47 (2)	773 (4)	3928 (9)	682 (14)
C16	-358 (2)	964 (5)	2347 (8)	683 (14)
C17	-787 (1)	38 (4)	2500 (8)	684 (13)
C18	-801 (2)	-1057 (4)	4267 (9)	733 (15)
C19	-394 (2)	-1224 (4)	5813 (9)	719 (15)
C26	-1204 (2)	1198 (6)	-765 (9)	811 (17)

Table 8. Atomic fractional coordinates ( $\times 10^4$ ) and  $U_{eq}$  values ( $\text{\AA}^2 \times 10^4$ ) for compound 12

	x	y	z	$U_{eq}$
O1	-1263 (3)	3824 (8)	-5010 (5)	1212 (24)
O2	-1940 (3)	5803 (7)	-5895 (5)	1192 (22)
N1	94 (2)	2565 (5)	-393 (4)	623 (15)
N2	-557 (2)	3335 (5)	-508 (5)	591 (15)
N3	-1687 (3)	4941 (7)	-4838 (6)	833 (21)
C1	341 (3)	2015 (6)	1118 (6)	551 (18)
C2	948 (3)	969 (7)	1335 (7)	685 (22)
C3	1186 (4)	499 (8)	2844 (6)	740 (24)
C4	869 (4)	1024 (9)	4100 (7)	778 (28)
C5	275 (4)	2003 (9)	3848 (7)	811 (30)
C6	7 (3)	2525 (8)	2419 (6)	605 (19)
C7	487 (4)	2248 (10)	-1776 (7)	730 (27)
C13	-829 (3)	3824 (6)	-1856 (7)	625 (21)
C14	-1535 (3)	4708 (6)	-1894 (6)	628 (19)
C15	-1828 (3)	5123 (7)	-480 (7)	694 (23)
C16	-2477 (4)	5963 (8)	-457 (9)	834 (27)
C17	-2870 (4)	6427 (9)	-1803 (10)	905 (30)
C18	-2580 (3)	6094 (8)	-3256 (9)	832 (26)
C19	-1927 (3)	5226 (7)	-3277 (6)	663 (20)

tions arising from the IR spectra of the cited compounds are:

(i)  $\nu(\text{N-H})$  stretching vibrations. The values range from 3310 to 3320  $\text{cm}^{-1}$  for the unsubstituted 1 and 7 and for the substituted 10, 18 and 21 derivatives. Compound 4 absorbs to higher frequencies (3355  $\text{cm}^{-1}$ ). A decrease of  $\nu(\text{NH})$  frequency is found in the derivatives 17 and 18 owing to the combined electronic and structural effects. In compound 18 there is the possibility of intermolecular H bonding (Vickery *et al.*, 1985) and therefore a considerable decrease of  $\nu(\text{NH})$  (3265  $\text{cm}^{-1}$ ) is seen compared with the unsubstituted hydrazone 1. A slight shift of NH absorption is registered for derivative 17, where the  $-\text{NO}_2$  group is involved in an intramolecular H bond, introducing a certain amount of strain in the hydrazono framework (Drew *et al.*, 1984); the same behaviour is shown by compound 16 which has  $\nu(\text{NH})$  at 3302  $\text{cm}^{-1}$  (X-ray analysis on 12 also evidences the presence of a strain in the phenylhydrazono group). In derivative 14,

with the nitro group in the *para* position of the benzaldehyde ring,  $\nu(\text{NH})$  is at  $3308\text{ cm}^{-1}$  without an appreciable influence of the mesomeric effect. In compounds 19 and 20 (as with 14), CT interactions are not possible owing to the additional electronic ( $\text{NO}_2^-$ ) and strain ( $o\text{-NO}_2^-$ ) effects. As far as solvent effects are concerned, we note a decrease of NH absorption frequency as solvent polarity increases (a shift in the range of  $15\text{ cm}^{-1}$  is often observed going

from benzene to chloroform), see Table 11. This situation (also verified in the *p*- $\text{NO}_2$  14 and 18 derivatives or *o*- $\text{NO}_2$  16 derivative) is not present in compounds 17, 19 and 20 where the intramolecular  $-\text{NO}_2 \cdots \text{H}-\text{N}=\text{C}$  bond prevents any solvent participation. Neither H bonding nor strain effects can be identified in the derivative 10 that, consequently, shows a normal absorption at  $3318\text{ cm}^{-1}$ ;

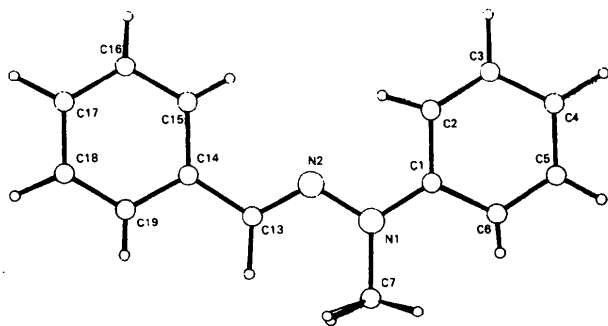


Fig. 1. Benzaldehyde methyl(phenyl)hydrazone (compound 2).

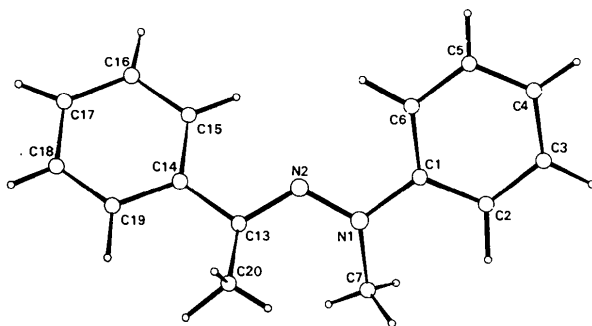


Fig. 2. Acetophenone methyl(phenyl)hydrazone (compound 5).

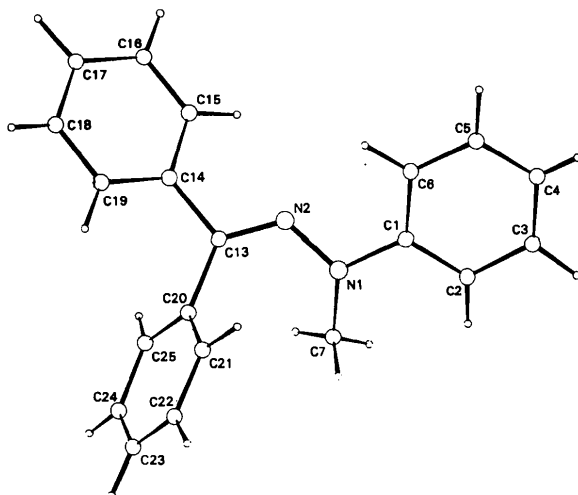


Fig. 3. Benzophenone methyl(phenyl)hydrazone (compound 8).

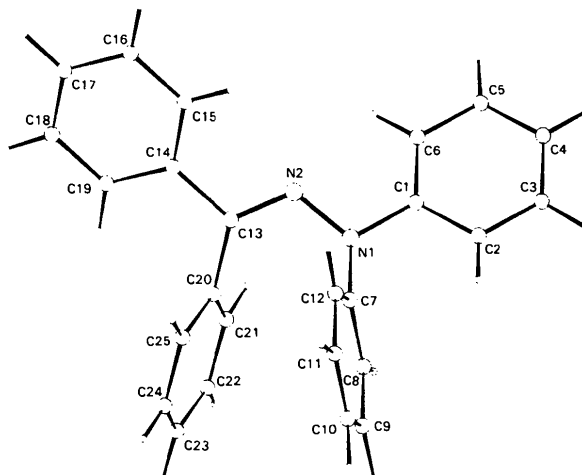


Fig. 4. Benzophenone diphenylhydrazone (compound 9).

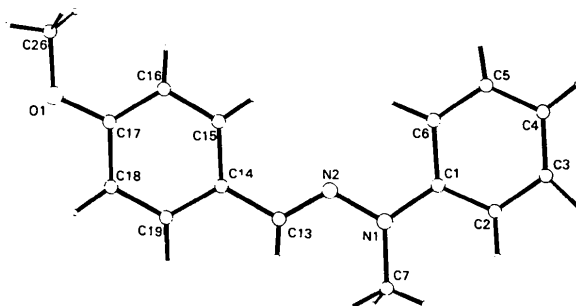


Fig. 5. *p*-Methoxybenzaldehyde methyl(phenyl)hydrazone (compound 11).

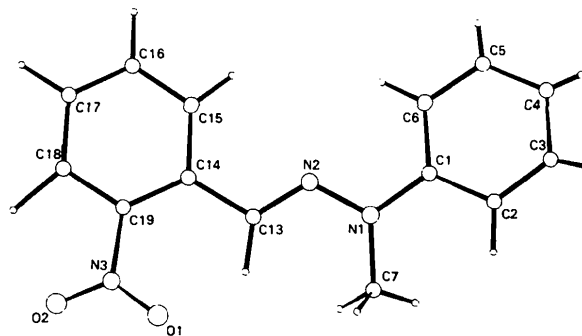


Fig. 6. 2-Nitrobenzaldehyde methyl(phenyl)hydrazone (compound 12).

Table 9. Selected bond distances (Å) and angles (°)

	(2)	(5)	(8)	(9)	(11)	(12)
O1-N3						1.216 (8)
O2-N3						1.214 (7)
O-C17					1.358 (4)	
O-C26					1.408 (6)	
N1-N2	1.358 (6)	1.307 (6)	1.377 (3)	1.381 (2)	1.373 (5)	1.358 (5)
N1-C1	1.381 (7)	1.445 (6)	1.416 (3)	1.435 (2)	1.410 (5)	1.418 (5)
N1-C7	1.496 (9)	1.475 (7)	1.459 (4)	1.453 (2)	1.444 (7)	1.461 (7)
N2-C13	1.292 (7)	1.350 (6)	1.294 (3)	1.312 (2)	1.262 (6)	1.292 (7)
N3-C19						1.462 (7)
C13-C14	1.472 (7)	1.436 (6)	1.490 (3)	1.482 (2)	1.450 (6)	1.492 (8)
C13-C20		1.475 (8)	1.504 (3)	1.483 (2)		
C17-O-C26					117.9 (3)	
N2-N1-C1	117.6 (4)	115.7 (4)	113.5 (2)	113.8 (1)	116.6 (3)	116.1 (4)
N2-N1-C7	120.2 (5)	121.4 (4)	122.0 (2)	119.1 (1)	121.4 (4)	121.0 (4)
C1-N1-C7	122.1 (5)	118.9 (4)	119.9 (2)	118.7 (1)	121.8 (4)	122.8 (5)
N1-N2-C13	120.9 (4)	121.3 (4)	122.9 (2)	118.9 (1)	121.8 (3)	119.7 (4)
O1-N3-O2						123.9 (5)
O2-N3-C19						117.9 (5)
O1-N3-C19						118.2 (5)
N1-C1-C2	120.8 (5)	121.2 (4)	121.1 (2)	120.5 (1)	121.9 (4)	120.9 (5)
N1-C1-C6	123.8 (5)	119.8 (4)	120.4 (2)	120.4 (1)	120.1 (3)	120.9 (5)
N1-C7-C8				119.8 (1)		
N1-C7-C12				120.3 (1)		
N2-C13-C14	119.4 (4)	113.7 (4)	127.7 (2)	115.6 (1)	121.6 (4)	117.0 (5)
N2-C13-C20		120.0 (4)	114.5 (2)	125.2 (1)		
C14-C13-C20		118.4 (5)	117.6 (2)	118.7 (1)		
C13-C14-C15	122.8 (5)	121.1 (4)	120.0 (2)	119.7 (2)	122.2 (3)	119.3 (5)
C13-C14-C19	119.5 (5)	121.4 (4)	121.4 (2)	120.4 (2)	121.1 (4)	124.1 (5)
N3-C19-C18						114.3 (5)
N3-C19-C14						123.5 (5)
C13-C20-C21			121.0 (2)	120.6 (1)		
C13-C20-C25			120.9 (2)	120.7 (1)		
Averaged C-C distances (Å) and C-C-C angles (°) in phenyl rings						
C1...C6	1.383 (6)	1.395 (6)	1.390 (5)	1.390 (1)	1.380 (6)	1.376 (10)
C7...C12				1.393 (2)		
C14...C19	1.381 (6)	1.385 (7)	1.387 (4)	1.387 (2)	1.394 (4)	1.402 (6)
C20...C25			1.395 (5)	1.388 (3)		
C1...C6	119.9 (10)	119.9 (3)	119.7 (4)	120.0 (2)	119.8 (8)	119.8 (11)
C7...C12				119.8 (2)		
C14...C19	119.8 (9)	119.7 (8)	120.0 (4)	119.9 (1)	119.8 (8)	119.9 (10)
C20...C25			120.0 (5)	119.8 (3)		

Table 10. Angles (°) between least-squares planes

Planes: A, C1...C6; B, C14...C19; C, C20...C25; D, C7...C12;  
E, C1,N1,N2; F, N1,N2,C13.

	(2)	(5)	(8)	(9)	(11)	(12)
A-B	4.5 (2)	38.2 (2)	48.1 (1)	51.8 (1)	5.8 (1)	7.3 (2)
A-C			77.1 (1)	86.7 (1)		
A-D				99.6 (1)		
A-E	3.5 (3)	6.9 (3)	17.5 (2)	21.6 (1)	4.8 (2)	11.5 (3)
A-F	3.8 (3)	13.2 (3)	24.2 (2)	27.7 (1)	5.6 (2)	10.4 (3)
B-C			73.3 (4)	77.8 (1)		
C-D				88.1 (1)		
C-F			64.3 (2)	73.3 (1)		
D-E				67.6 (1)		

Table 11. Characteristic absorption bands (cm<sup>-1</sup>) for the investigated phenylhydrazones in the solid state and in solution with different solvents

	Solid state			Solution		
	N-H	H-C=N	C=N	Benzene	DCE	CHCl <sub>3</sub>
(1)	3320/12	2976	1560	3329	3334	3342
(2)		2960	1558			
(3)		2957	1560			
(4)	3355		1570	3361	3363	3374
(5)			1568			
(6)			1567			
(7)	3322		1558	3342	3337	3343
(8)			1566			
(9)			1550			
(10)	3318	2978	1560	3328	3336	3346
(11)		2960	1558			
(12)		2966	1565/70			
(13)						
(14)	3308		1558/65	3323	3331	3344
(15)						
(16)	3302		1575	3317	3331	3337
(17)	3300		1570/80	3315	3315	3314
(18)	3265		1560/70	3326	3336	3343
(19)	3330		1565/70	3338	3338	3338
(20)	3305		1563/68	3317	3320	3325
(21)	3318		1568/78	3338	3334	3340

(ii) The  $\nu(\text{C}=\text{N})$  absorptions are characterized by a low-intensity band ranging from 1555 to 1570 cm<sup>-1</sup>. Even though the literature (Fabian, Legrand & Poiner, 1956; Tanner, 1959) discusses the difficulty in localizing this band [owing to the closeness of strong aromatic  $\nu(\text{C}=\text{C})$  absorption], these bands are clearly resolvable with a high-resolution spectrophotometer. It is interesting to note that the phenylhydrazones showing

the  $\nu(\text{C}=\text{N})$  band close to  $1560\text{ cm}^{-1}$  are able to undergo CT interaction with organic acceptors and those absorbing close to  $1570\text{ cm}^{-1}$  are not. An exception is shown by compound 4 and, to some extent, by derivative 21. It is also interesting to note that the  $\nu(\text{C}=\text{N})$  absorption in all nitro-substituted phenylhydrazones is split into two frequency values.

It is not easy to correlate the frequency values of other bands in the spectra with the type of substituent in the hydrazone molecule.

Previous studies suggested that the formation and the stability of a molecular association between a molecule of phenylhydrazone and an organic acceptor was related to the inertness of the donor to undergo side reactions and to the position and nature of the substituent bonded to the hydrazone group or to the aromatic rings present.

Some striking differences in the possibility of CT bonding between similar phenylhydrazones could not be explained on the basis of common electronic or steric factors. For example, from experimental findings we can argue:

(i) that the amounts of CT bonding of benzaldehyde phenylhydrazone derivatives are characterized by the sequence:  $11 > 10 > 2 > 3 \gtrsim 1 > 15 > 14 > 18 \gtrsim 21$  (no CT interaction was found using as donors the compounds 17 or 19);

(ii) that CT bonding can occur with the simple acetophenone or benzophenone phenylhydrazones but not with the corresponding methylphenyl- (5 and 8) or diphenylhydrazones (6 and 9).

According to the charge-transfer theory (Foster, 1969; Yarwood, 1973), the formation of a CT bond is closely related to the effectiveness of interaction between the orbitals of the active sites of the donor and the acceptor molecules. Hydrogen bonding between donor and acceptor is a particular, and quite common, case of a molecular association.

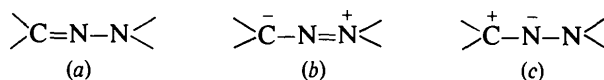
The acceptor properties of quinones are dependent not only on their lowest unoccupied  $\pi$  levels (affording  $\pi$ - $\pi$  interactions) but also on the unshared electron pairs of O and N atoms (with the possibility of CT bonding) (Hansen, 1968).

The occurrence of H bonding in our case cannot be excluded but experimental results [for example, the fact that benzaldehyde methyl(phenyl)hydrazone 2 forms a stronger complex with chloranil than benzaldehyde phenylhydrazone 1 does] show that this is not the main interaction. At this point it appears plausible that the active donor site in the phenylhydrazone molecule is the  $\text{C}=\text{N}$  group.

Comparison of the equilibrium constants for H bonding between *p*-nitrophenols and alkyhydrazones with the protonation constants of the latter compounds (together with calculations of the electrostatic potentials on the N atoms) indicates that the complexation occurs at the imine group and not on the amine N atom

(Zverev, Stolyarov, Yakupova & Kitaev, 1981) and the possibility of interactions with planar acceptors like tetracyanoethylene (Fatiadi, 1986) or chloranil (Prout & Kamenar, 1973) is closely related to its planarity and charge density.

The amount of charge density in the  $\text{C}=\text{N}$  group is dependent on the possibility of interaction between the non-bonding electrons of the terminal N atom and the  $\text{C}-\text{N}$   $\pi$  bond [contributing structure (b)].



On the other hand, ultraviolet studies (Iffland, McAneny & Weber, 1969) on phenylhydrazones demonstrate that the chromophore  $\text{C}=\text{N}-\text{N}$  of compounds 1, 4, 7 and 2 exhibits nearly the same spectrum and consequently the effect of the alkyl group in 2 is negligible.

In tetrasubstituted phenylhydrazones, the spectrum of the chromophore is quite different and this cannot be ascribed to the electronic properties of the new substituent [in this case the rotation about the  $\text{N}-\text{N}$  linkage is restricted and the contributing structure (b) is unfavoured and the structure (c) is the only one probable]. Similar results can be visualized from X-ray and FT-IR determinations on our phenylhydrazones. For example, the  $\nu(\text{C}=\text{N})$  band shows the same frequency absorption for trisubstituted phenylhydrazones while with tetra- or *ortho*- $\text{NO}_2$ -substituted phenylhydrazones the absorptions move to higher frequencies; at the same time, structural determinations evidence the existence of a certain strain around the  $\text{>C}=\text{N}-\text{N}<$  skeleton with the last two classes of compounds. From the above results it can be ruled out that in CTC interactions trisubstituted hydrazones with an *o*- $\text{NO}_2$  group on the aromatic ring have the same behaviour as tetrasubstituted ones: the strain introduced in the hydrazone skeleton by H bonding between the  $\text{NO}_2$  group and the amine N or aldehyde H atoms is equivalent to that enhanced by the fourth substituent on the hydrazono group. Also, in *p*- $\text{NO}_2$ -substituted hydrazones, the formation of CT bonding is more evident when the electron-withdrawing group is present on the benzaldehyde rather than on the phenyl hydrazone ring [favouring, in the former case, the structure (b)].

All experimental reports fully agree with the hypothesis that what determines the particular UV, IR and structural features (and consequently the possibility of obtaining CT interactions) is closely related to the steric interference of substituents at the C and terminal N atoms. Other reports of UV (Adembri, Sarti-Fantoni & Belgodere, 1966) or IR (Zverev, Stolyarov, Yakupova & Kitaev, 1975; Braude, Sondheimer & Forbes, 1954) determinations on similar



compounds are in accord with the above arguments. It is also interesting that tetracyanoethylene shows better complexing properties than chloranil (Table 1): this is not surprising owing, other things being equal, to the higher electron affinity of the former (2.2 eV) with respect to the latter acceptor (1.7 eV) (Briegleb, 1964).

In conclusion it can be pointed out that in phenylhydrazones the possibility of obtaining a CT interaction is firstly related to the absence of a discrete amount of strain on the hydrazono group that, consequently, may exist in a planar structure that allows conjugation in the group. Mesomeric and inductive effects of the substituents can only contribute to the amount and to the stability of the complex.

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## Crystal Structure and Photochemistry of Four $\alpha$ -Cycloalkyl-*p*-chloroacetophenones

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### Abstract

The photochemical fragmentation or cyclization reactions of  $\alpha$ -cycloalkylacetophenones have been studied by crystal-structure analyses of four chloro derivatives with varying cycloalkyl-ring sizes, and by correlation of crystal- and molecular-structure parameters with

photochemical behaviour. Crystal data are:  $T = 295$  K,  $\text{Mo } K\alpha_1$ ,  $\lambda = 0.70930$  Å, or  $\text{Cu } K\alpha_1$ ,  $\lambda = 1.54056$  Å;  $\alpha$ -cyclobutyl-4-chloroacetophenone [1-(4-chlorophenyl)-2-cyclobutylethanone],  $\text{C}_{12}\text{H}_{13}\text{ClO}$ ,  $M_r = 208.69$ , monoclinic,  $C2/c$ ,  $a = 26.403$  (9),  $b = 10.903$  (4),  $c = 7.800$  (2) Å,  $\beta = 103.94$  (3)°,  $V = 2179.3$  (12) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.272$  g cm<sup>-3</sup>,  $\mu =$