Molecular complexes of hydrazones—VIII. Nitrofluorenes and arylhydrazones*

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Abstract—Nitrofluorenes form π - π complexes with a series of hydrazones both in solution and in the solid state. The properties of the complexes, discussed on the basis of u.v.-vis and FT-i.r. data, suggest the presence of weak interactions, as confirmed by the formation constants and X-ray analysis. The presence of some degree of charge transfer is confirmed by ESR determinations. The X-ray analysis of the complex of benzaldehydediphenylhydrazone with 2,4,7-trinitrofluorenone is also reported.

INTRODUCTION

Hydrazones behave as electron donors in intermolecular complexes with organic electron acceptors in the solution of many solvents; electronic and steric factors influence the stability as well as the amount of the formed complex [1]. The formation constants (in various solvents such as benzene, dichloromethane, carbon tetrachloride, etc.) of all the complexes known to date are characterized by low values (in the range of $1-51 \text{ mol}^{-1}$) and no complex can be isolated in the solid state [2]. 2,4,7-Trinitrofluorenone, I, and 9dicyanomethylene-2,4,7-trinitrofluorenone, II, are moderately large π -acceptors in the formation of charge transfer complexes with a variety of donors, including aromatic hydrocarbons [3], indoles [4], quinolines [5] and dimethylaniline derivatives [6]. No report may be found on molecular interactions between acceptors I and II with acyclic substrates bearing imino groups. In this work we describe the synthesis and the preparation of solid complexes of I and II with a number of arylhydrazones (preliminary results, indicating that anils are also able to form complexes with I and II, will be described elsewhere).

EXPERIMENTAL

Hydrazones were prepared following known procedures [7]. 2,4,7-Trinitrofluorenone (I) and 9-dicyanomethylene-2,4,7-trinitrofluorenone (II) were Aldrich RP-ACS reagents and were recrystallized by appropriate solvents before use. All solvents were Fluka RP-ACS grade.

General procedure for the synthesis of all cited complexes

Almost saturated equimolar solutions of the donor and acceptor in absolute ethanol were mixed at room temperature and left standing until discrete amounts of crystals were obtained (from 1 to 10 days). The solids were filtered and recrystallized by ethanol. Analytical data and melting points are reported in Table 1. In a second procedure, on mixing saturated solutions of the reagents in MeCN, powder complexes precipitated that had the same chemical and spectroscopic characteristics as the ones obtained in ethanol.

Ultraviolet-visible spectrophotometric measurements on the complex of benzaldehydemethylphenylhydrazone with TNF (or DTF) in benzene: K determinations

From stock solutions of freshly prepared hydrazone, approximately 2.86×10^{-1} M, and TNF, approximately 8.92×10^{-3} M (hydrazone approximately 1.92×10^{-1} M and DTF approximately 6.30×10^{-3} M), eight samples were prepared by mixing 0.250, 0.500, 0.750, 1.00, 1.25, 1.50, 1.75, 2.00 cm³ of donor solution and 1.00 cm³ of TNF (or DTF) solution. Five different samples of each mixture were prepared for a total of 40, on which the determination of absorbance (d), at the λ_{max} of the complex, was performed at 25.0°C. A linear correlation was obtained plotting $[A]_0 l/d$ against $1/[D]_0$, where $[A]_0$ and $[D]_0$ indicate the total concentration of the acceptor and of the donor, l = 1 cm is the light path and d is the absorbance (optical density). In all cases the correlation coefficients (r) were greater than 0.9999.

X-ray analysis of the complex 8.TNF

Complex 8.TNF: $C_{19}H_{16}N_2/C_{13}H_5N_3O_7$, monoclinic, $P2_1/a$, $M_r = 587.5$, a = 7.635(2), b = 41.841(3), c = 8.727(2)Å, $\beta = 94.81(3)^\circ$, V = 2778.1(1)Å³, Z = 4, $D_x = 1.40$ g cm⁻³, λ (CuK_a) = 1.5418Å, $\mu = 8.05$ cm⁻¹, F(000) = 1216. The structure was solved by direct methods and refined by blockmatrix least-squares, to give R = 0.045 and $R_w = 0.051$ for 2847 reflections above 2σ (*I*).

The diffraction data were measured at room temperature on a Siemens AED single crystal diffractometer equipped with an IBM PS2/30 personal computer employing a prismatic crystal $0.3 \times 0.5 \times 0.6$ mm. The unit cell parameters resulted from a least-squares fit to angular values of 30 reflections ($11 \le 9 \le 45^\circ$) accurately well centered on the diffractometer with a routine which repeatedly improves the angular values to have the maximum of the peak until the angles are moving not more than 0.01°. The reflections were measured using a modified version [8] of the Lehmann and Larsen method [9]. One check reflection was monitored every 50 measurements and its count did not alter noticeably. The intensities were corrected for Lorentz and polarization effects but not for absorption. A total of 5753 reflections were collected (index range h - 26/26, k 0/7, l 0/12) in the 9 range of 3-70°; 3054 of them were observed having $I > 2\sigma$ (1): 2859 were unique $(R_{int} = 0.013)$ and used in the refinement. The structure was solved by direct methods with MULTAN80 [10] and refined through block-matrix least-squares at the

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beginning with the isotropic thermal parameters (R = 0.15), and then with anisotropic ones (R = 0.081). All the hydrogen atoms were found in a difference Fourier map calculated at this stage and refined isotropically. The function minimized was $\Sigma \ \omega \Delta F^2$; unit weights were used at the beginning of the refinements while at the final stages the weighting scheme w $= 1/(\sigma^2 F + 0.004796 F^2)$ was employed. In the final cycles 12 reflections were omitted because they were probably affected by extinction.

The highest peaks of the final ΔF maps were 0.29 eÅ ⁻³. The final refinement converged to R = 0.045, $R_w = 0.051$ and S = 0.68. The maximum shifts/e.s.d. value in the final cycle was 0.62. Atomic scattering factors are those of SHELX76.*

All the calculations were performed on an IBM PS2/80 with the CRYSRULER package [11].

Physical measurements

Solid-state i.r. spectra were obtained using a Nicolet Fourier Transform Infrared 20-SX Spectrometer equipped with a Spectra Tech. Multiple Internal Reflectance "Collector"; u.v.-vis determinations in solution were carried out on a Perkin-Elmer Model 554 spectrophotometer equipped with a MgW-K2R thermostatting system for circulating water. Mass spectra were obtained with a Hewlett Packard model 5895 B spectrometer while ESR spectra were recorded on a Varian E-4 ESR spectrometer using a deaerated two-leg inverted cell described previously [12]. Melting points were determined on a micro hot-stage point apparatus and are uncorrected.

RESULTS AND DISCUSSION

Tables 1 and 2 respectively report analytical and u.v.-vis, i.r. data of the complexes. Among the investigated hydrazones, compound 7 did not interact with I and II, while in the case of complexes of 6 with I and II, only the first one could be sufficiently purified for analysis. The complexes of hydrazones with I show, in the u.v.-vis region, two bands (that are absent in the starting acceptor) in the range 450-500 and Acceptor, A



525-630 nm, while those with II show a single CT band in the range 580-795 nm; the determination of λ_{max} for complexes 6.II, 9.I and 13.II were impossible because of strong overlapping with other bands. The broadness of CT bands is responsible for some degree of uncertainty in the λ_{max} determinations.

In Fig. 1, a plot of v_{CT} for complexes of TNF against v_{CT} for the corresponding complexes of DTF with donors 1-5, 8, 10-12 is shown. A linear relationship is found in complexes from donors 1, 2, 10-12. The scatter of points 3-5 and 8 can be explained with a considerable deviation from planarity in the corresponding hydrazones, which introduces some degree of steric hindrance and lowers the complex stability in solution [2]. The plot does not have a unit gradient, because rather different orbitals (mainly in the acceptors) are involved in the formation of both groups of complexes [13].

Electron releasing substituents force the λ_{max} to shift to higher wavelengths: surprisingly a positive bathochromic shift is also observed in the complex 8.I, where the phenyl ring on the amino nitrogen should induce a blue shift for inductive and steric effects. In all cases the CT bands of complexes with DTF are found at longer wavelengths as a consequence of the higher π -acid strength of II ($E = \alpha - 0.21 \beta$), with respect to I ($E = \alpha - 0.30 \beta$), assuming, as is evident, that almost the same bonding (e.g. $\pi - \pi$, $n - \pi$ etc.) occurs in the two classes of complexes [3a, 14]. In the case of DTF, the complexes absorb at higher wavelengths on going from benzaldehyde- to acetophenone- through benzophenonephenylhydrazone.

The carbonyl stretching band (Table 2) of acceptor I does not show regular behaviour on going from the free to the complexed state: with donors 2 and 3 an expected red shift is the consequence of a higher polarization and an increased charge density on the C=O group due to the formation of a sandwich π - π structure with some charge transfer. In all other

^{*}Lists of structure factor amplitudes and thermal parameters are available from one of the authors (G.B.) on request.

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Comp.	Analysis,	Found	(Calc.)%	цъ	M.W.	Mol. formula	Comp.	Analysis,	Found	(Calc.)%	ц.п	M.W.	Mol. formula
	C	н	z	(°C)				С	Н	Z	(°C)		
I.I	60.98	3.42	13.63	155-7	511.29	C ₂₆ H ₁₇ N ₅ O ₇	1.11	62.04	3.09	17.47	138	559.33	C ₂₉ H ₁ ,N ₇ O ₆
	(61.07)	(3.32)	(13.69)				1	(62.30)	(3.04) (3.04)	(17.53)			
2.1	61.83	3.50	13.42	139	525.30	C27H19N5O7	2.11	62.97	3.25	16.98	134-6	573.34	C30H19N7O6
	(61.73)	(3.62)	(13.33)					(62.84)	(3.31)	(17.10)			:
3.1	65.08	3.52	12.06	147	587.35	C32H21N5O7	3.II	65.97	3.29	15.53	184-5	635.39	C35H21N,O6
	(65.43)	(3.57)	(11.92)					(66.15)	(3.30)	(15.43)			
4.1	62.69	3.92	11.62	233-5	601.36	C33H23N5O7	4.11	66.67	3.57	15.16	191-3	649.40	C ₃₆ H ₂₃ N ₇ O ₆
	(65.90)	(3.82)	(11.64)					(66.58)	(3.54)	(15.10)			
5.1	61.54	3.68	13.18	147-50	525.30	C27H19N5O7	5. II	62.84	3.26	17.03	160-1	573.34	C ₃₀ H ₁₉ N ₇ O ₆
	(61.73)	(3.62)	(13.33)					(62.84)	(3.31)	(17.10)			
6.1	62.01	4.03	13.10	235	539.31	C ₂₈ H ₂₁ N ₅ O,							
	(62.35)	(3.89)	(12.98)										
8.1	65.12	3.68	11.79	128-9	587.35	C ₃₂ H ₂₁ N ₅ O ₇	8.11	66.29	3.28	15.42	186-9	635.39	C ₃₅ H ₂₁ N ₇ O ₆
	(65.43)	(3.57)	(11.92)					(66.15)	(3.30)	(15.43)			
9.I	66.04	3.81	11.45	151-5	601.36	C ₃₃ H ₂₃ N ₅ O,	11.e	66.47	3.51	15.22	172-3	649.40	C ₃₆ H ₂₃ N ₇ O ₆
	(65.90)	(3.82)	(11.64)					(66.58)	(3.54)	(15.10)			
10.1	60.06	3.5	12.88	128-9	540.30	C2,H1,N,O8	10.11	61.13	3.22	16.54	183-5	589.34	C ₃₀ H ₁₉ N ₇ O ₇
	(60.01)	(3.51)	(12.96)					(61.13)	(3.22)	(16.63)			
11.1	58.79	3.76	12.32	138	569.31	C28H21N5O	11.11	59.98	3.42	15.71	175-8	619.35	C ₃₁ H ₂₁ N ₇ O ₈
	(29.06)	(3.68)	(12.30)					(60.11)	(3.39)	(15.83)			
12.1	59.71	3.49	12.80	124-8	540.30	C,,H,,N,O,	12.II	61.17	3.22	16.51	182-4	589.34	C ₃₀ H ₁₉ N ₇ O ₇
	(60.01)	(3.51)	(12.96)					(61.13)	(3.22)	(16.63)			
13.I	56.95	2.84	14.95	137-9	556.29	C, HINO,	13.11	58.21	2.49	18.01	222	604.34	C ₂₉ H ₁₆ N ₈ O ₈
	(56.13)	(2.87)	(15.10)					(57.63)	(2.65)	(18.54)			

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	0CH3						1245 1248	1252, 1249 1254	1253, 1238	
	NO _{2sym}	1359, 1343 1346 1351, 1342	1338, 1344 1345 1342	1341 1348 1341	1357, 1345 1349 1341	1341 1311 1342	1344 1344 1344 1345	1345 1344	1351 1351 1345	1347
	NO _{2asym}	1543, 1518 1548, 1525 1545, 1538, 1528	1545, 1531 1538 1543, 1526	1540 1526 1533	1525 1540, 1529 1541, 1533 1533, 1522	1540, 1524 1548, 1525 1540, 1540	1540, 1521 1529 1529	1544 1528	1543 1538 1574	1527 1527 1537, 1528
nfrared	C=N	1565 1562	1560 1559 1559 1558	1558 1548 1551, 1563	1559 1558, 1564 1559 1558	1559 1557 1559	1552 1559 1579 1553	1568 1562, 1543 1568	1559 1557	1560 1558 1577, 1545
	C=0	1730 1739, 1733	1728	1729 1737	1734 1735	1732	1733	1724	1734 1733	een1 1729
	C≣N	2253	2230 2228	2225	2249, 2240	2228	2224 2229	2227, 2255	2226	2226
	OCH,						2837 2839 2839	2840 2840 2839	2838 2839	
	HN	3313, 3307 3306	3308, 3313 3321 3310 3321 3310	3317 3317	3350, 3333 3340, 3327		3317, 3312 3315 3322	3324, 3310 3315, 3229 3267 3303, 3279	3278 3309 3301, 3286	3295 3297
	Compound			2311 114 114	14 v 13 v 2	611 881 9811		11 11 11 11 12	12.1 13.11 13.	13.11 15 151

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Fig. 1. Plot of v_{CT} for the series of complexes of DTF and TNF with donors 1-5, 8, 10-12.

complexes the anomalous shift [15] to higher wavenumbers can be due to an $n-\pi$ interaction [16], made possible by a carbonyl group that is partially present as an anion radical (see ESR), so acting as a donor [17]: both effects being present in the complexes, the final vCO will be a compromise.

The question of whether the carbonyl group may be involved in some hydrogen bonding with the donor is not relevant, owing to the fact that, for example, hydrazone 2 forms with a quinono acceptor, like chloranil, a stronger complex than does hydrazone 1 [13]. The small shifts mean that the carbonyl group is not individually involved in the CT transition and the absorption is a consequence of the electronic changes which occurred in the molecule as a whole; as a matter of fact, the C=O bond lengths are unaffected in the complexes, as seen by X-ray analysis: in any case the above results are in agreement with recent reports [18]. Concerning the NO_{2asym} and NO_{2sym} vibrations in the complexes, an absorption at lower wavenumbers confirms the acceptor character of the nitro group. The C≡N absorption of II is moderately shifted to lower wavenumbers in the complexes $(15-20 \text{ cm}^{-1})$ excluding any influence of the anion radical. The hydrazono C=N absorptions in the complex fall at lower wavenumbers with respect to the free donors; the shifts are very small in the case of 3-6, 9, 13 with I, showing that the CT transition comes from the amino nitrogen rather than from the C=N group, because the steric situation around the C=N carbon in these donors prevents it from acting as main donor [19].

Characteristic absorptions (in solid) and chemical shifts (in solution) of OCH₃, in the complexes of donors 10-12, do not present any differences with respect to the free donors, as should be expected from the lowering of the ionization potential [20]. Nevertheless, an influence of the methoxy groups in the complex formation has been demonstrated with different acceptors [2] and also qualitatively verified in this work.

Because of solubility difficulties, the determination of the equilibrium constant (K) in benzene was limited to complexes 2.I and 2.II at 25° C, using the

Benesi-Hildebrand equation [21], K values (2.22 ± 0.09 and $4.39 \pm 0.21 \, \text{lmol}^{-1}$ for the complexes 2.1 and 2.11, respectively) are in the range of those (in tetrahydrofuran) reported in the literature for similar systems [22].

The stoichiometry of all complexes (D/A = 1/1) was determined by elemental analysis (Table 1) and mass spectra, which at low energy fields did not show any adduct but only the peaks of the components [23].

ESR signals of the radical anion corresponding to the acceptor* were easily detected, either on mixing MeCN solutions of the reagents or dissolving the crystalline complex in dimethyl sulfoxide. Even if some radical character in a complex may be induced by the ionizing power of the solvent [15], the content of the anion radical in the complexes of II with the hydrazones was higher than that in the complexes of I with the same donors.

The final atomic fractional coordinates of the complex hydrazone 8.TNF are listed in Table 3, and bond distances and angles are given in Table 4. A projection of the molecule with an arbitrary numbering scheme is shown in Fig. 2. The geometry of the fluorenone skeleton is consistent with that reported in other fluorenone derivatives [24-26]. In particular, the fluorenone moiety as a whole is quasi planar, 1.8 (1) and 1.9 (1)° being the dihedral angles formed by the two six-membered rings with the central one and $3.2 (1)^{\circ}$ being that between the two benzene rings. These values are comparable with those of 0.90, 0.75 and 1.65° found in 2,7-diamino-9-fluorenone [27] and of 0.5, 1.4 and 1.6° in 4-isopropyl fluorenone [28]. The three nitro groups are tilted by 4.4 (3), 5.2 (3) and 3.9 $(3)^{\circ}$ with respect to the mean fluorenone system plane. Each individual ring is planar with very small r.m.s. deviations. Bond distances of the two benzene rings average 1.384(6) and 1.382(5) A while the Cl-C2, C1-C13 and C7-C8 distances are close to the values of 1.48 Å accepted for a single bond between two sp^2 carbons [29, 30]. As observed in 4-isopropylfuorenone [28] or in 9-fluorenone [25], the internal angles of the benzene rings may be divided into three groups: those with an average of 118.0(3), $116.2(4)^{\circ}$ at C3, C6, and C8, C12, those with an average of 119.6 (4), 120.5 (6)° at C5, C7, and C9, C10 and, finally, those with mean values of 122.3 (3), 123.4 (3)° at C2, C4, and C11, C13. These not great but significant differences in the internal angles of the benzene rings together with those remarkable in their bond distances, are probably due to the deformations in the carbon atoms hybridization by the condensed five-membered ring.

As already observed in other phenylhydrazones [1, 31], the absence of the NH fragment in the aliphatic chain nullifies the possibility of intra- or intermolecular hydrogen bonds often observed in these kinds of derivatives. The phenylhydrazone as a whole is, as

^{*}The radical anions were identified by comparing their ESR spectra with those obtained from I and II, and ButOK in DMSO.

X/A 01 2027 (3)	Y/B	Z/C	T , / T ,
O1 2027 (3)	- /	2,0	$U_{\rm eq}/U_{\rm iso}$
01 1010/0	1484(1)	6630(2)	772(7)
02 - 1912(5)	735(1)	2848(3)	1558 (17)
-2383(4)	260(1)	3585 (3)	1284(13)
04 1245(7)	292(1)	10857(4)	2033 (25)
$O_5 = 2442(5)$ $O_6 = 5572(3)$	430(1)	12927(3)	1256(14)
07 $5592(4)$	1391(1)	13687(3)	902(10) 1350(14)
N1 $-1767(4)$	524(1)	3792(3)	936(12)
N2 2040(4)	483(1)	11622(3)	785(10)
N3 5145(4)	1489(1)	12410(3)	801 (11)
C1 1799(3)	1246(1)	7380(3)	570 (8)
C2 847 (3)	953(1)	6878(3)	535 (8)
$C_3 = -23(4)$	891(1)	5470(3)	632(10)
-781(4)	363(1)	5258(3) 6377(4)	648 (10)
$C_{6} = -650(4)$	427(1)	7810(3)	617(10)
C7 959(3)	726(1)	8072(3)	521 (8)
C8 1966(3)	878(1)	9431(3)	509 (8)
C9 2508 (4)	789 (1)	10938 (3)	577 (9)
C10 3539(4)	988(1)	11903(3)	653 (10)
C11 4014(4)	1283(1)	11380(3)	614 (9)
C12 3473 (4)	1390(1)	9930(3)	580 (9)
$V_{13} = 24/3(3)$	1184 (1)	8998(3)	527(8)
N4 = 6453(5) N5 $7908(3)$	1009(1) 1377(1)	8037(2)	629(7) 561(7)
C14 6854(3)	1266(1)	7853(3)	543(8)
C15 6284(3)	931(1)	7895(3)	514(8)
C16 5331 (4)	800(1)	6622(3)	586 (8)
C17 4770(4)	485(1)	6632(4)	681 (11)
C18 5159(4)	299(1)	7916(4)	694(11)
C19 = 6084(4)	428(1)	9191 (4) 0184 (3)	690(10) 581(0)
$C_{20} = 0044(4)$	1619(1)	11519(3)	626 (9)
C22 10798 (4)	1733(1)	12762(3)	738(12)
C23 11585 (5)	2025(1)	12712(4)	913(13)
C24 11332(6)	2202(1)	11408 (5)	1116(17)
C25 10277(5)	2093(1)	10146(4)	947 (15)
C26 94/1(4) C27 7628(2)	1800(1)	10199(3)	601 (9)
$C_{27} = \frac{7028(3)}{8227(4)}$	1903(1) 1922(1)	//00(3) 6310(3)	578(8)
$C_{29} = \frac{6227}{7355(4)}$	2107(1)	5196(3)	713(10)
C30 5907 (4)	2276(1)	5523(4)	763 (10)
C31 5307(5)	2262(1)	6968 (4)	824(13)
C32 6175(4)	2075(1)	8110(4)	715(11)
H3 $-7(38)$	104(7)	472 (34)	826 (95)
H5 $-129(44)$	17(7)	612(36) 872(22)	832(102)
H10 391 (37)	23 (0) 91 (7)	872 (33) 1292 (33)	740(85)
H12 379(37)	158(7)	960(33)	756 (90)
H14 643 (31)	139 (5)	703 (27)	580 (68)
H16 514(35)	92(6)	575 (31)	708 (83)
H17 418(41)	40 (6)	578 (34)	854 (91)
H18 468 (41)	8(8)	793 (34)	888 (103)
H19 03/(40) H20 718(25)	29(8)	1014(43)	1068(118)
$H_{20} = 118(55)$ $H_{21} = 920(36)$	141(7)	1158(33)	703(83) 787(92)
H22 1101 (43)	160(7)	1373 (42)	983 (110)
H23 1240 (39)	209 (7)	1363 (34)	978 (91)
H24 1192(48)	239 (9)	1140 (39)	1081 (121)
H25 1018(52)	221 (9)	918 (45)	1352(139)
H28 918(39) H20 770(39)	1/9(7)	613(33)	862 (96)
H30 531(36)	211(/) 240(6)	418(54) 471(31)	049 (90) 875 (84)
H31 430(43)	237(7)	721 (34)	935(106)
H32 574 (35)	206 (6)	913 (31)	733 (83)

Table 3. Atomic fractional coordinates (×10⁴ for heavy atoms, ×10³ for H atoms) and U_{eq} (×10⁴ Å²) or U_{iso} (×10⁴ Å²)

expected, not perfectly planar, $9.2(2)^{\circ}$ being the dihedral angle between the aromatic (C15 \cdots C20) ring and the C14, N5, N4 plane. The bond lengths for the N4-C26 and N4-C27, N4-N5, N5-C14 are in general a little different from the mean distances of 1.41, 1.34 and 1.31 Å assumed from the literature data [32] for



Fig. 2. Projection of benzaldehydediphenylhydrazone. 2,4,7-Trinitrofluorenone complex.

similar distances. The N5–C14 length of 1.277(3) Å is clearly indicative of a double bond, as found in *N*benzoylphenylhydrazone and *N*-benzoyl-*p*-bromophenylhydrazone [31] or in molecular orbital calculations [33]. All these data seem to indicate a certain degree of conjugation of the aliphatic chain with the aromatic rings.

The angle between the two gem phenyl rings [91.6 $(1)^{\circ}$] is comparable with that [99.6 $(1)^{\circ}$] found in benzophenonephenylhydrazone. One of them (C21... C26) lies practically in the plane of the rest of the molecule [tilted by 7.1(1)] while the second one forms a dihedral angle of 97.7 (1) with the rest of the molecule.

In the crystals the molecules (Fig. 3) are joined together by Van der Waals' forces only. The molecules are packed in parallel planes along the a and c directions. The distance between these planes is about 3.3 Å.

Some interesting considerations may be deduced from the geometry of the complexes: the D-A-D-A stacks are faced in such a way that the 2-NO₂ group superimposes the nitrogen atoms N4-N5 of the hydrazone. Taking this into account, the $n-\pi$ or $\pi-\pi$ interactions between the N4-N5-C14 and the 2-NO₂aromatic ring frames appear the most important ones. This hypothesis is also supported by the analysis of computed stabilization energies in similar systems (complexes between II and quinolines) where a minimum of energy configuration is achieved when the 2-NO₂ group superimposes the donor center [5].



Fig. 3. Packing of benzaldehydediphenylhydrazone. 2,4,7-Trinitrofluorenone complex.

Table 4. Bond distances (Å) and angles (°)

01-C1	1.212(4)	C12-C13	1.372(5)
O2-N1	1.206(5)	N4-N5	1.367(1)
O3-N1	1.208(6)	N4-C26	1.406(3)
O4-N2	1.177(6)	N4-C27	1.438(4)
O5-N2	1.176(4)	N5C14	1.277(3)
O6-N3	1.206(6)	C14C15	1.469 (6)
O7–N3	1.209 (4)	C15-C16	1.389(4)
N1-C4	1.459 (4)	C15-C20	1.388(5)
N2-C9	1.469(6)	C16-C17	1.386(6)
N3-C11	1.472 (5)	C17-C18	1.376(5)
C1–C2	1.473(5)	C18-C19	1.377 (5)
C1-C13	1.485(4)	C19-C20	1.374(6)
C2–C3	1.372(4)	C21–C22	1.379(4)
C2–C7	1.407(5)	C21–C26	1.380(5)
C3C4	1.373(6)	C22C23	1.364(6)
C4–C5	1.375(5)	C23–C24	1.358(6)
C5-C6	1.391 (4)	C24–C25	1.386(6)
C6-C7	1.384(6)	C25–C26	1.374 (6)
C7–C8	1.500(4)	C27–C28	1.376(4)
C8–C9	1.395(4)	C27-C32	1.378(5)
C8-C13	1.399(6)	C28-C29	1.376(5)
C9-C10	1.382(5)	C29–C30	1.363 (5)
C10C11	1.375(6)	C30-C31	1.379(5)
C11-C12	1.372(4)	C31-C32	1.391 (5)
C3-H3	0.92(3)	C21-H21	0.95(3)
C5-H5	0.96(3)	C22-H22	0.99(3)
C6H6	1.08(3)	C23–H23	1.00(3)
C10-H10	0.95(3)	C24-H24	0.93 (4)
C12-H12	0.92(3)	C25-H25	0.99(4)
C14-H14	0.93(2)	C28-H28	0.92(3)
C16-H16	0.92(3)	C29-H29	0.97(3)
C17H17	0.90(3)	C30-H30	0.96(3)
C18H18	0.96(3)	C31-H31	0.93(3)
C19-H19	0.99 (4)	C32–H32	0.97(3)
C20-H20	0.89 (3)		.,
O2N1O3	123.7(3)	C11-C12-C13	116.8(3)
O3-N1-C4	118.9(3)	C8-C13-C12	124.6(2)
O2-N1-C4	117.4(3)	C1-C13-C12	125.8(3)
O4-N2-O5	120.1 (4)	C1-C13-C8	109.6(2)
O5-N2-C9	120.3(3)	C26-N4-C27	122.1(2)
O4-N2-C9	119.5(3)	N5-N4 -C27	120.1 (1)
O6N3O7	124.0(3)	N5-N4 -C26	116.3(1)
07-N3-C11	118.0(3)	N4-N5 -C14	119.8(1)
O6-N3-C11	117.9(2)	N5-C14-C15	119.9(2)
01-C1-C13	127.1 (3)	C14-C15-C20	122.0(2)
O1-C1-C2	127.8(2)	C14-C15-C16	119.5(3)
C2-C1-C13	105.1 (2)	C16-C15-C20	118.4 (4)
C1-C2-C7	110.1(2)	C15-C16-C17	120.8(2)
C1C2C3	127.8(3)	C16-C17-C18	119.8(3)
C3-C2-C7	122.0(3)	C17-C18-C19	119.8(3)
C2-C3-C4	117.3(2)	C18-C19-C20	120.5(3)
N1-C4-C3	118.8(2)	C15-C20-C19	120.7(3)
C3-C4-C5	122.4(3)	C22-C21-C26	120.3 (3)
N1-C4-C5	118.7(3)	C21-C22-C23	120.9 (2)

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