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Bonding in Phenylhydrazones: X-Ray Crystal Structure and Theoretical Calculations Involving (*E*)-Acetophenone Phenylhydrazone

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Summary. Semiempirical (PM3 type) calculations have been carried out on the *E* isomer of acetophenone phenylhydrazone and extended to include acetophenoneimine and phenylhydrazone. The optimized structure of acetophenone phenylhydrazone has also been compared with the solid state structure obtained from the results of an X-ray crystal structure determination. The crystals are monoclinic, space group $P2_1/c$, $a = 5.520(2)$ Å, $b = 8.944(3)$ Å, $c = 23.591(8)$ Å, $\beta = 90.28(3)°$, and $V = 1164.7(7)$ Å^3. The final R value is 0.0549 for 1097 reflections with $F > 3\sigma(F)$. The structure possesses a planar conformation and both N atoms possess trigonal-planar geometries. Results of the theoretical calculation are in good agreement with those obtained from the crystallographic data and indicate that conjugation between the hydrazone region and the phenyl rings plays a significant role in favoring a planar molecular conformation and has a significant perturbing influence on the bond lengths and angles associated with the hydrazone C=N–N atoms. A Mulliken analysis for the structure gives bond orders of 1.77 and 1.10 for the formally double bonded C–N and single-bonded N–N atoms, respectively.

Keywords. *E*-Acetophenone phenylhydrazone; Crystal structure; Theoretical calculations.

Bindungen in Phenylhydrazonen. Röntgenstrukturanalyse und theoretische Berechnungen an (*E*)-Acetoxyphenon-phenylhydrazin

Zusammenfassung. Es wurden semiempirische PM3-Typ-Berechnungen für das *E*-Isomere von Acetophenon-phenylhydrazon durchgeführt und dann auf Acetophenonimin und Phenylhydrazon ausgeweitet. Die optimierte Geometrie von Acetophenon-phenylhydrazon wurde mit der Kristallstruktur dieser Verbindung verglichen. Die Kristalle sind monoklin, Raumgruppe $P2_1/c$, $a = 5.520(2)$ Å, $b = 8.944(3)$ Å, $c = 23.591(8)$ Å, $\beta = 90.28(3)°$ und $V = 1164.7(7)$ Å^3. Der endgültige R-Wert für 1097 Reflexe mit $F > 3\sigma(F)$ war 0.0549. Die Struktur besitzt eine planare Konformation und beide N-Atome haben trigonal-planare Geometrien. Die Ergebnisse der theoretischen Berechnungen sind in guter Übereinstimmung mit jenen aus den kristallographischen Daten und zeigen, daß die Konjugation zwischen dem Hydrazonteil und den Phenylringen eine signifikante Rolle bei der planaren Konformation trägt und auch einen entscheidenden Einfluß auf Störungen bei Bindungslängen und -winkel in der Hydrazongruppierung C=N–N hat. Eine Mulliken-Analyse der Struktur ergab Bindungsordnungen von 1.77 bzw. 1.10 für die formale Doppelbindung C–N bzw. die Einfachbindung N–N.

Introduction

Compounds containing the triatomic C–N–N bridge belong to a large class of materials known collectively as hydrazones [1]. They are related to azines by the presence of a C–N double bond, but are distinguished by the presence of two nitrogen atoms. Characteristic features of this class of molecules include strong intermolecular hydrogen bonding interactions in hydrazones derived from α-dicarbonyl compounds [1], *E*/*Z*-diastereomerization [2–4], as well as polymorphism which may be responsible for the appearance of various colors occasionally observed [5].

Although a detailed theoretical study of bonding in phenylhydrazones has not been carried out, the crystal structures of a large number of phenylhydrazones have been determined and several interesting structural features have emerged. In virtually all instances the hydrazone molecule adopts a planar conformation. When aromatic substituents or functional groups capable of conjugating with the C=N bond are present, the C–N portion of the hydrazone linkage becomes lengthened and is accompanied by a commensurate decrease in the N–N bond length. Studies of the C–N bond stretching frequencies have been correlated with the bond length and used to provide estimates of the C–N bond order in a number of systems; correlations such as these involving hydrazones have provided values ranging from 1.80 to 1.90 [6]. Less attention has been paid to the N–N bond in these compounds, although empirical relationships between the crystallographically observed N–N bond length and bond order have been established [7]. An intuitive argument is that these variations can be attributed to conjugation involving the lone pair electrons on the amine nitrogen and the π-electrons of the aromatic rings. Although reasonable, such arguments remain somewhat unsatisfying and, to date, a detailed theoretical analysis of the bonding in hydrazones has not been carried out.

In this paper the solid state structure of (*E*)-acetophenone phenylhydrazone is reported using data obtained from an X-ray crystal structure determination and compared with the results obtained from a theoretical (PM3 type) semiempirical calculation. Important features regarding the conformation of this structure in light of information concerning the molecular orbitals derived from these semiempirical calculations are discussed and, for the first time, quantitative data concerning bonding in the hydrazone region is presented, as well as energies of the pertinent MO's.

Experimental Part

(*E*)-Acetophenone phenylhydrazone was prepared by reacting 1.8 g (15 mmol) of acetophenone dissolved in 20.0 ml of ethanol with 1.0 g (7 mmol) of phenylhydrazine hydrochloride dissolved in 5.00 ml of H_2SO_4 along with 5.00 ml of H_2O. The mixture was allowed to stir overnight at room temperature after which well-formed transparent crystals were obtained in 39% yield (based on the amount of phenylhydrazone used) following recrystallization from 95% ethanol.

Crystal Data

$C_{14}H_{14}N_2$, $M = 210.3$; crystal dimensions ca. 0.4 × 1.2 × 0.8 mm, space group $P2_1/c$, $a = 5.520(2)$ Å, $b = 8.944(3)$ Å, $c = 23.591(8)$ Å, $\beta = 90.28(3)°$, $V = 1164.7(7)$ Å^3, $D_{calc} = 1.199\ \mathrm{g\,cm^{-3}}$, $Z = 4$. μ(Mo-

Kα) = 0.67 cm^{-1}, $F(000) = 448$. Monoclinic symmetry was suggested on the basis of the interaxial angles and confirmed by axial rotation photographs. Refined cell parameters were based on the setting angles of 25 high-angle reflections with $15° < 2\theta < 30°$.

Data Collection, Structure Solution and Refinement

Data collection was carried out at ambient temperature using the ω-scanning technique and a Siemens R3m/v diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Scan rate variable, 3–15° min^{-1}, scan range 1.4° in ω. A total 1528 unique independent reflections were collected. The data were corrected for Lorentz and polarization effects, but not absorption. Three standards measured every 100 data showed no significant variations in intensity over the period of data collection. The Shelxtl-*Plus* collection of crystallographic software was used for the structure solution and refinement [8]. Scattering factors for all atoms, including terms for anomalous dispersion, were taken from the International Tables for X-ray Crystallography [9]. The structure was solved using direct methods and refined using a full-matrix least-squares refinement procedure. Refinement was based on F using weights of the form $w^{-1} = \sigma^2(F) + 0.0003F^2$. Convergence to conventional R values of $R = 5.49\%$ and $wR = 6.68\%$ was obtained using 146 variable parameters and 1097 reflections with $F > 3\sigma(F)$. Phenyl ring hydrogen atoms were placed in idealized positions with fixed isotropic $U = 0.080$ Å^2. Final atomic positional parameters for the structure are given in Table 1 and pertinent bond angles and distances are summarized in Table 2. A view of the structure illustrating the atomic numbering scheme is provided in Fig. 1. A list of structure factors, hydrogen atom positional parameters and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Center (CDCC). Additional data about the crystal structure of (*E*)-acetophenone phenylhydrazone can be obtained from the authors.

Theoretical Calculations

Quantum mechanical calculations for structure optimization were performed using the PM3 parameters (DFG convergence) of the MOPAC 5.1 package adapted for the Macintoch by Tektronix (CAChe system) [10]. Reliability of the method was confirmed by comparing the values for bond distances and angles obtained from the fully optimized structure with those obtained from the X-ray crystal structure determination [11].

Results and Discussion

Structure Results

In this structure the two phenyl rings are essentially coplanar and are twisted with respect to each other by angle less than 4°. The central hydrazone region is also essentially coplanar with both phenyl rings and N(2) is displaced by less than 0.1 Å from the least-squares plane defined by the three atoms to which it is attached. The atoms associated with the N–N=C linkage display interaxial angles that deviate only slightly from that expected for atoms possessing ideal trigonal-planar geometries, ranging from 116.0(3)° to 122.3(3)°. The 1.363(4) Å N(1)–N(2) distance in this structure is well within the range typically observed in other phenylhydrazones, but is considerably shorter than the 1.45 Å N–N bond length in hydrazine [12]. The C=N bond length in this structure measures 1.287(4) Å and is longer than the 1.27 Å value typically observed in azines. Structural details associated with the phenyl rings are unexceptional and will not be discussed further, except to note that rather substantial variations in the C–C bond lengths have been occasionally observed in

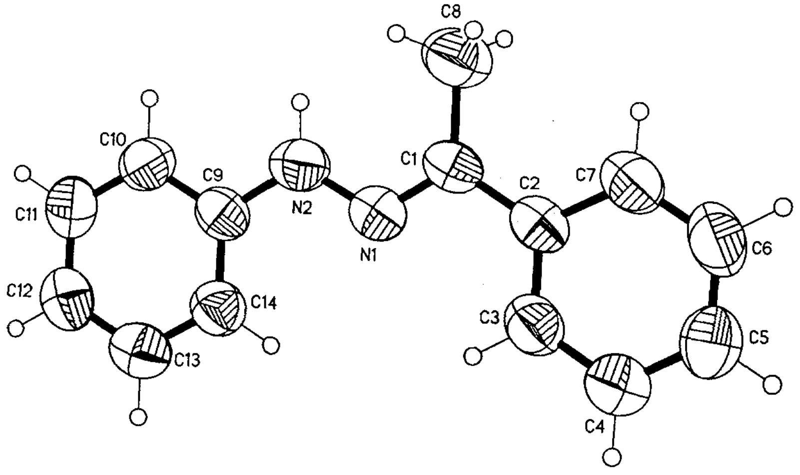

Fig. 1. A view of the structure illustrating the atomic numbering scheme

Table 1. Atomic fractional co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
N(1)	708(4)	4221(3)	1660(1)
C(2)	−457(5)	3588(3)	733(1)
C(1)	−837(5)	4450(3)	1259(1)
C(14)	4021(6)	3769(4)	2548(1)
C(9)	2111(6)	4756(4)	2593(1)
N(2)	464(5)	4993(3)	2154(1)
C(10)	1847(6)	5578(4)	3088(1)
C(13)	5654(6)	3625(4)	2990(2)
C(7)	−2061(6)	3657(4)	278(2)
C(3)	1525(6)	2665(4)	673(2)
C(12)	5403(7)	4455(4)	3477(2)
C(11)	3483(7)	5420(4)	3525(1)
C(6)	−1686(7)	2844(5)	−205(2)
C(5)	282(7)	1927(4)	−258(2)
C(4)	1883(6)	1849(4)	185(2)
C(8)	−2888(6)	5545(4)	1306(2)

the structures of other phenylhydrazones containing intramolecular hydrogen bonds, as well as those containing nitro groups.

Theoretical Considerations of Bonding

The results of the semiempirical PM3 calculations are in good agreement with the structural data derived from the crystal structure determination. A view showing the superposition of the crystallographically determined structure and the optimized

Table 2. Molecular geometries

(i) Bond distances (Å)			
N(1)–C(1)	1.287(4)	N(1)–N(2)	1.363(4)
C(2)–C(1)	1.477(4)	C(2)–C(7)	1.390(5)
C(2)–C(3)	1.378(5)	C(1)–C(8)	1.502(5)
C(14)–C(9)	1.380(5)	C(14)–C(13)	1.380(5)
C(9)–N(2)	1.390(4)	C(9)–C(10)	1.389(5)
C(10)–C(11)	1.374(5)	C(13)–C(12)	1.375(5)
C(7)–C(6)	1.367(6)	C(3)–C(4)	1.379(5)
C(12)–C(11)	1.372(5)	C(6)–C(5)	1.367(6)
C(5)–C(4)	1.368(5)		
(ii) Bond angles (deg.)			
C(1)–N(1)–N(2)	118.7(3)	C(1)–C(2)–C(7)	122.3(3)
C(1)–C(2)–C(3)	120.9(3)	C(7)–C(2)–C(3)	116.8(3)
N(1)–C(1)–C(2)	116.0(3)	N(1)–C(1)–C(8)	123.2(3)
C(2)–C(1)–C(8)	120.8(3)	C(9)–C(14)–C(13)	120.0(3)
C(14)–C(9)–N(2)	122.6(3)	C(14)–C(9)–C(10)	119.0(3)
N(2)–C(9)–C(10)	118.3(3)	N(1)–N(2)–C(9)	119.5(3)
C(9)–C(10)–C(11)	120.4(3)	C(14)–C(13)–C(12)	120.8(3)
C(2)–C(7)–C(6)	121.4(3)	C(2)–C(3)–C(4)	121.3(3)
C(13)–C(12)–C(11)	119.4(3)	C(10)–C(11)–C(12)	120.4(3)
C(7)–C(6)–C(5)	121.3(4)	C(6)–C(5)–C(4)	118.1(3)
C(3)–C(4)–(5)	121.1(3)		

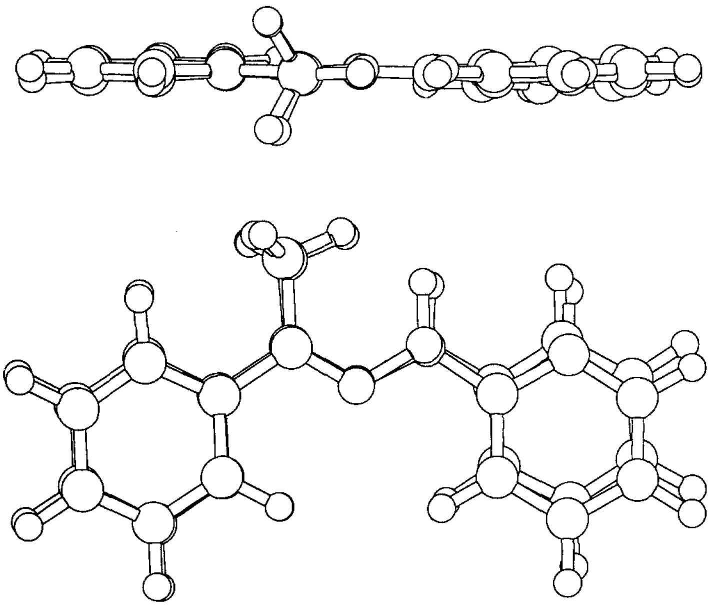

Fig. 2. Two views showing the superposition of the optimized structure (PM3 type calculation) with the crystallographically determined structure

structure is shown in Fig. 2. All calculated bond distances associated with the two phenyl rings have acceptable values, ranging from 1.387–1.405 Å and 1.094–1.097 Å for C–C and C–H bonds, respectively. The dihedral angle about the N–N and C=N bonds from the structurally optimized calculation *and* the observed X-ray structure data are within 0.5° of planarity.

Of particular interest are the calculated parameters associated the hydrazone portion of the molecule; in Tables 3 and 4 are presented summaries comparing the calculated values with those determined experimentally along with their respective differences.

From these tables it is evident that the values obtained using the semiempirical PM3 calculation are in good agreement with those obtained by an X-ray crystal structure determination. Several features of the structure, however, merit discussion. These features include (1) the short N–N bond length, (2) the trigonal-planar geometry exhibited by N(1), and (3) the length of the C–N double bond.

These results can be rationalized if one considers that N(1) is best described as being an sp^2 hybrid. This is consistent with the observed trigonal planar geometry of N(1) and requires that the remaining electrons be placed in a p_z orbital. Delocalization of these p_z orbital electrons with the π orbitals on the adjacent phenyl ring and C=N atoms would then be maximized only when coplanarity of all atom groups is established. In addition to providing a motivating force behind a planar molecular structure, such delocalization would be expected have a significant perturbing effect on the observed pattern of bond lengths in the hydrazone region of the molecule.

Table 3. Selected bond lengths (Å), X-ray data, {theoretical calculations} and difference

	Observed	Calculated	Difference
N(1)–C(1)	1.287(4)	{1.314}	0.027
N(1)–N(2)	1.363(4)	{1.361}	−0.002
N(2)–C(9)	1.390(4)	{1.429}	−0.039
C(1)–C(2)	1.477(4)	{1.476}	−0.001
C(1)–C(8)	1.502(5)	{1.496}	−0.006

Table 4. Selected bond angles in degrees, X-ray data, {theoretical calculation} and difference

	Observed	Calculated	Difference
C(1)–N(1)–N(2)	118.7(3)	{122.6}	3.9
N(1)–C(1)–C(2)	116.0(3)	{117.2}	1.2
C(2)–C(1)–C(8)	120.8(3)	{118.7}	−2.1
N(1)–C(1)–C(8)	123.2(3)	{124.1}	0.9
N(1)–N(2)–C(9)	119.5(3)	{120.9}	1.4

In order to establish the importance of electron delocalization in the structure described here, PM3 calculations were extended to include phenylhydrazone, *Ph*NH–NH$_2$, as well as acetophenoneimine, *Ph*(*Me*)C=NH. In the case of phenylhydrazone, conjugation of the N–N atoms with the aromatic ring can be expected to be considerably less important and this is indeed born out in the calculated value of the N–N bond length which, at 1.447 Å (PM3 calculation), is appreciably longer than that observed in the title compound. Furthermore, the calculation shows that both nitrogens of *Ph*NH–NH$_2$ are *not planar* and show little, if any, sp^2 hybridization. With acetophenoneimine, conjugation between the phenyl ring and the C=N group is more important. The 1.289 Å C=N bond distance that was calculated is essentially identical the 1.287(4) Å C=N bond length observed in the title complex. These data are summarized in Table 5.

It is clear that electron delocalization is important in rationalizing the observed patterns of bond lengths in the phenylhydrazones. An inspection of the MO's for this system indeed bear this out, and for the question at hand only HOMO-4, HOMO-5 and HOMO-8 are relevant [13].

A view of the three pertinent MO's are given in Fig. 3. HOMO-4 and HOMO-5 are very close in energy (−10.59278 and −10.60937 eV, respectively) with coincident strong mixing of the lone pair of N(2). In HOMO-4 there is a large lobe associated with N(1) that is distinct from the MO's of π symmetry that extends over N–N=C atoms and includes C(2) of the phenyl ring. Very likely the lone pair of electrons

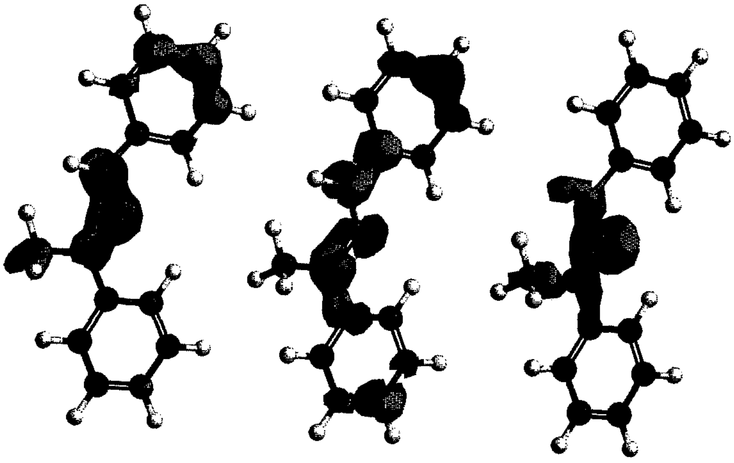

Fig. 3. A pictorial representation of HOMO's 4, 5 and 8 of the title compound

Table 5. N–N and C=N bond distances (Å)

	(*E*)-(C$_6$H$_5$)NH–N=CH(C$_6$H$_4$)(CH$_3$) X-ray	 PM3 (cal)	*Ph*NH–NH$_2$ PM3 (cal)	*Ph*(*Me*)C=NH PM3 (cal)
N–N	1.363	1.361	1.447	–
C=N	1.287	1.314	–	1.289

resides here. HOMO-5 is similar insofar as conjugation extends to include the C atoms of the phenyl rings. In this case, however, both phenyl rings are involved and there is a node between N(1) and N(2). In HOMO-8, MO formation involves principally the N–N=C atoms of the hydrazone linkage and is reminiscent of HOMO-1 of the allyl anion. Of the three HOMO's shown, it lies lowest in energy (-12.42254 eV) and clearly shows conjugation over the entire N–N=C backbone.

An exhaustive search through the crystallographic literature reveals that similar patterns of bond lengths and angles are observed in all hydrazones containing phenyl ring substituents. From the results of the theoretical calculations, it is evident that in hydrazones that electron delocalization plays an important role in defining the planar nature of these compounds, and is responsible for the interesting patterns of bond lengths and angles observed in this class of compounds. A Mulliken analysis for the structure described here gives a bond order of 1.77 for the formally doubly bonded C=N fragment and a bond order of 1.10 for the formally singly-bonded N–N atoms. The former calculated bond order is slightly less than that estimated from studies of C–N bond stretching frequencies. Both values, however, are consistent with the concept of partial delocalization of electron density over the N–N–C atoms.

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[13] For the title complex the HOMO is the 40th molecular orbital. For simplicity, the MO's have been numbered relative to the HOMO and LUMO: i.e. LUMO + *n* and HOMO-*n*, where *n* is a positive integer

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