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The Reaction of Sulphinylhydrazides with Aromatic Aldehydes, and the Geometrical Isomerism of Acylhydrazones

By P. Hope and L. A. Wiles

Acylhydrazones are formed by the condensation of sulphinylhydrazides with aromatic aldehydes. Their geometrical isomerism has been studied by infrared spectra.

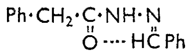
N-Sulphinyl-amines, $R{\cdot}N{:}SO$, and *N*-sulphinylsulphonamides, $R{\cdot}SO_2{\cdot}N{:}SO$, react with carbonyl compounds with the elimination of sulphur dioxide, and replacement of the carbonyl oxygen atom by the group $=NR'$ or $=N{\cdot}SO_2{\cdot}R'$.[1,2] *N'*-Sulphinylhydrazides, $R{\cdot}CO{\cdot}NH{\cdot}NSO$, are often unstable,[3] but the reaction of the more stable members with aromatic aldehydes has now been studied. The products are acylhydrazones (reaction 1). For comparison, the acylhydrazones were also obtained by the well-known reaction of acylhydrazides with the corresponding aromatic aldehydes (reaction 2). Compounds containing the group C=N can exist as geometrical isomers, but they are much more labile than the geometrical forms of ethylenic compounds.[4]

$$R{\cdot}CO{\cdot}NH{\cdot}N\boxed{SO + O}HC{\cdot}R' \longrightarrow R{\cdot}CO{\cdot}NH{\cdot}N{:}CHR' + SO_2 \quad (1)$$

$$R{\cdot}CO{\cdot}NH{\cdot}N\boxed{H_2 + O}HC{\cdot}R' \longrightarrow R{\cdot}CO{\cdot}NH{\cdot}N{:}CHR' + H_2O \quad (2)$$

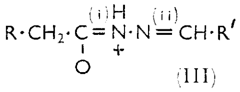
In the present work the condensation of *N'*-sulphinylphenylacetohydrazide with benzaldehyde gave benzaldehyde phenylacetylhydrazone, m. p. 139°. On raising the temperature the material solidified and remelted at 149°. Condensation of phenylacetohydrazide with benzaldehyde gave only the higher melting form.

Molecules of the *cis*-form (I) can have an intramolecular hydrogen bond, and Courtauld molecular models show that such a six-membered ring is likely. Many crystalline compounds with intramolecular C–H • • • O bonds are now recognised,[5] and in some of these the carbon atom of the CH group is activated by being directly attached to a more electronegative atom. Intermolecular hydrogen bonding of (I) through CO and NH groups is also likely. In the *trans*-form the intramolecular hydrogen bond cannot exist, and a dimerised cyclic form (II) is possible.



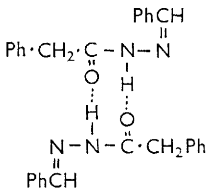
$$\begin{array}{l} Ph{\cdot}CH_2{\cdot}C{\cdot}NH{\cdot}N \\ \qquad\qquad \| \qquad\quad\ \| \\ \qquad\qquad O \cdots HCPh \end{array}$$

(I)



$$R{\cdot}CH_2{\cdot}\underset{\underset{O}{|}}{\overset{(i)H}{C}}=\underset{+}{N}{\cdot}N\overset{(ii)}{=}CH{\cdot}R'$$

(III)



$$\begin{array}{l} \qquad\qquad\qquad PhCH \\ \qquad\qquad\qquad\ \ \| \\ Ph{\cdot}CH_2{\cdot}C-N-N \\ \qquad\qquad \| \quad\ | \\ \qquad\qquad O \quad H \\ \qquad\qquad \vdots \quad\ \vdots \\ \qquad\qquad H \quad O \\ \qquad\qquad | \quad\ \ \| \\ \qquad\quad N-N-C{\cdot}CH_2Ph \\ \qquad\quad \| \\ \quad PhCH \end{array}$$

(II)

The infrared spectra, determined in the solid state, give an indication of their stereochemical relationship. Both forms have an NH band at 3175 cm.$^{-1}$. This is compatible with the hydrogen-bonded structures indicated,[6a] and the identical position of the bands excludes the possibility of geometrical isomerism around the amide group. The bands (cm.$^{-1}$) which show relevant differences are:

	γ(CH)	γ(CO)	γ(CN)
Low-melting form	3000	1667, 1661	1603w, 1563w
High-melting form	—	1674, 1669, 1661, 1654	1606w, 1565m

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[1] G. Kresze and R. Albrecht, *Angew. Chem.* (*Internat. Edn.*), 1962, **1**, 595.

[2] G. Schulz and G. Kresze, *Angew. Chem.* (*Internat. Edn.*), 1963, **2**, 736.

[3] P. Hope and L. A. Wiles, *J. Chem. Soc.*, 1965, 5386.

[4] D. Y. Curtin and J. W. Hausser, *J. Amer. Chem. Soc.*, 1961, **83**, 3474.

[5] D. J. Sutor, *J. Chem. Soc.*, 1963, 1105.

[6] L. J. Bellamy, " Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., 1958, (*a*) p. 208, (*b*) p. 216.

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The positions of the CN bands are not altered on deuteration; they are, therefore, not caused by the amide II band.[6b]

The methidene, =CH, band is likely to be present in (II) but absent from (I). The carbonyl stretching region of (I) will be more complex than that of (II) by virtue of the inter- and intra-molecular associations. The splitting of the CN band is to be expected since (III) is a mesomeric form of the acylhydrazone and the molecule has two different CN groups (i, ii). In one isomer the lower-frequency band is more intense than in the other one. This band we attribute to bond (i) with the positive charge on the nitrogen atom; similar shifts to lower frequency have been previously observed.[7] In (I) the carbonyl oxygen atom will utilise part of the negative charge for intramolecular hydrogen bonding, and the contribution of (III) will be enhanced with consequent intensification of the band due to (i). Conversely, in (II) the band will be weaker.

On the above evidence we ascribe a *trans* configuration (II) to the lower-melting form, and a *cis* arrangement (I) to the higher-melting.

TABLE 1

Infrared spectra (cm.$^{-1}$) of acylhydrazones ($R{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CH{\cdot}R'$)

No.	R	R′	CO bands	CN bands	Isomer
1	Phenyl	Phenyl	1667, 1661	1603w, 1563w	*trans*
2	,,	,,	1674, 1669, 1661, 1654	1606w, 1565m	*cis*
3	,,	*p*-Nitrophenyl	1674, 1667, 1663	1599m, 1565m	*cis*
4	,,	*m*-Nitrophenyl	1672, 1667	1600w, 1565w	*trans*
5	,,	*p*-Chlorophenyl	1678, 1669, 1660	1556w, 1541m	*cis*
6	,,	*m*-Chlorophenyl	1676, 1667, 1662	1559m, 1563m	*cis*
7	,,	*o*-Chlorophenyl	1680, 1673, 1667	1599w, 1565m	*cis*
8	,,	*p*-Tolyl	1674, 1667	1598w, 1565w	*trans*
9	,,	*o*-Hydroxyphenyl	1674, 1665, 1660	1610w, 1567w—m	*cis*
10	,,	Piperonyl	1667	1599w, 1566w	*trans*
11	,,	4-Hydroxy-3-methoxyphenyl	1674, 1667, 1660, 1650, 1643	1599m, 1567m	*cis*
12	Naphthyl	Phenyl	1684, 1677, 1670	1603w, 1567m	*cis*
13	n-Hexyl	,,	1684, 1677, 1670, 1665	1610w, 1567w	*cis*
14	,,	*p*-Nitrophenyl	1684, 1677, 1670, 1665	1660w, 1587m	*cis*
15	,,	*p*-Chlorophenyl	1684, 1677, 1670, 1665	— , 1567m	*cis*

TABLE 2

Preparation of acylhydrazones from sulphinylhydrazides or hydrazides

				Found (%)					Required (%)			
No.	Method *	Yield (%)	M. p.	C	H	Cl	N	Formula	C	H	Cl	N
1	A	70	139 and 149° (lit., 154°) §	75·4	5·7		11·9	$C_{15}H_{14}N_2O$	75·6	5·9		11·7
2	B	70	148	76·4	5·8		11·9	,,	,,	,,		,,
3	A	71	180 and 191	63·9	4·7		15·1	$C_{15}H_{13}N_3O_3$	63·5	4·6		14·9
	B	71	181 and 191	—	—		—	,,	—	—		—
	B †	74	191	—	—		—	,,	—	—		—
4	A	92	191	63·0	5·1		15·4	,,	63·5	4·6		14·9
5	A	100	167 (lit., 167°) ¶	65·5	5·0	13·3	10·9	$C_{15}H_{13}ClN_2O$	66·0	4·8	13·0	10·3
	B	100	167	67·1	4·7	13·1	10·9	,,	,,	,,	,,	,,
6	A	77	168	66·7	5·0	12·8	10·3	,,	,,	,,	,,	,,
7	A	62	166	66·3	4·7	12·8	10·5	,,	,,	,,	,,	,,
8	A	50	143	77·5	6·2		11·4	$C_{16}H_{16}N_2O$	76·2	6·4		11·1
	B	84	144	76·2	6·5		11·2	,,	,,	,,		,,
9	A	52	186 (lit., 188°) §	71·1	5·7		10·9	$C_{15}H_{14}N_2O_2$	70·9	5·5		11·0
10	A	75	216 (lit., 219°) ¶	68·1	4·7		10·3	$C_{16}H_{14}N_2O_3$	68·1	5·0		9·9
11	A	42	122 (decomp.)	67·1	5·7		10·2	$C_{16}H_{16}N_2O_3$	67·5	5·6		9·9
	B	84	122 (decomp.)	—	—		—	,,	—	—		—
12	A	100	213	79·4	5·7		9·8	$C_{19}H_{16}N_2O$	79·2	5·6		9·7
	B	100	213	—	—		—	,,	—	—		—
13	A ‡	50	70	73·2	9·1		12·5	$C_{15}H_{22}N_2O$	73·2	8·9		11·4
	B	50	70	—	—		—	,,	—	—		—
14	A †	46	143	61·7	7·2		15·5	$C_{15}H_{21}N_3O_3$	61·8	7·2		14·5
	B	100	146	—	—		—	,,	—	—		—
15	A ‡	46	81	63·5	7·5	12·6	9·6	$C_{15}H_{21}ClN_2O$	64·1	7·5	12·7	10·0
	B ‡	19	86	—	—		—	,,	—	—		—

* Recrystallised from ethanol unless stated otherwise. † From benzene. ‡ From light petroleum (b. p. 60—80°). § T. Curtius and E. Boetzelen, *J. prakt. Chem.*, 1901, **64**, 317. ¶ Ng. Ph. Buu-Hoï, Ng. D. Xuong, Ng. H. Nam, F. Binon, and R. Royer, *J. Chem. Soc.*, 1953, 1358.

We also decide the stereochemical nature of the other acylhydrazones (Table 1) from their infrared CO and CN bands. The methidene band is sometimes obscured by aromatic CH or aliphatic CH_2 bands, and its use for this identification is more limited.

The factors which influence the relative stabilities of the *cis*- and *trans*-forms are (a) steric hindrance, and (b) the acidity of the ethylenic hydrogen atom. Steric hindrance and increase in acidity will both favour the *cis*-form. The effect of (a) is shown in Nos. 7, 9, and 12. Courtauld models reveal that *ortho*-substituents (Nos. 7

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[7] J. D. S. Goulden, *J. Chem. Soc.*, 1953, 997.

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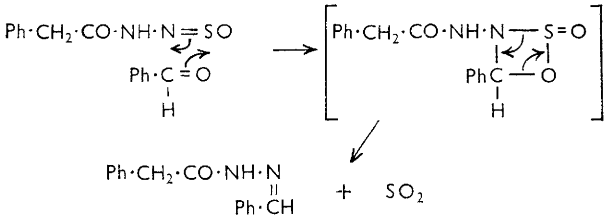
and 9) lead to overcrowded *trans* structures. No. **11** will consist of molecules associated through the *p*-hydroxy-group, and this will exclude the *trans*-form. The effect of (b) is evident in the remaining compounds. An electron-attracting substituent in the ring derived from the aromatic aldehyde will favour the *cis*-form (Nos. 3, 5, 6, and 7), and an electron-donating group will favour the *trans* (Nos. 8 and 10). Aliphatic sulphinylhydrazides have an increased charge on the carbonyl oxygen atom,[3] so that the compounds derived from these (Nos. 13—15) are *cis*, the electron-attracting *para*-substituent in Nos. **14** and **15** giving further help.

The formation of the less thermally stable *trans*-isomer from the reaction of *N'*-sulphinylphenylacetohydrazide and benzaldehyde (No. 1) indicates that combination proceeds through a cyclic intermediate of the type suggested for the reaction of *N*-sulphinylsulphonamides with sulphoxides [2] and α-diketones.[8]



The acylhydrazone from the condensation of *N'*-sulphinylphenylacetohydrazide with *p*-nitrobenzaldehyde (No. 3) has two polymorphic modifications (m. p. 180 and 191°). Heating, grinding, and crystallisation of the lower-melting form gives the higher-melting modification. The modifications therefore gave identical infrared spectra. Recrystallisation of the higher-melting from benzene converts it into the lower-melting type. Polymorphism was also observed with acylhydrazones (Nos. **14** and **15**).

EXPERIMENTAL

The sulphinylhydrazides were obtained as previously described.[3] Melting points were determined on a Kofler hot bench. Infrared spectra were measured for mulls in hexachlorobutadiene on a Grubb–Parsons Spectromaster.

General Methods for the Preparation of Acylhydrazones.—(A) *From the sulphinylhydrazide.* The sulphinylhydrazide and the aromatic aldehyde (50% excess) were heated together until sulphur dioxide ceased to be evolved. The product was recrystallised.

(B) *From the hydrazide.* The hydrazide and aromatic aldehyde (50% excess) were refluxed in ethanol (1 hr.). On cooling, the acylhydrazone crystallised.

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Swindon, Wilts. [5/780 *Received, July 23rd,* 1965]

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[8] G. Kresze, D. Sommerfeld, and R. Albrecht, *Chem. Ber.*, 1965, **98**, 601.