

AROMATICITY AND TAUTOMERISM—VII¹

EMPIRICAL RESONANCE ENERGY AND CONJUGATION ENERGY OF PYRAZOLE AND ISOXAZOLE FROM HEATS OF DEHYDRATION DATA

ANDREW V. CHAPMAN, MICHAEL J. COOK* and ALAN R. KATRITZKY*
School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, England

MICHAEL H. ABRAHAM and ANGELA F. DANIL DE NAMOR
Department of Chemistry, University of Surrey, Guildford GU2 5XH, Surrey, England

and

LILANE DUMONT and JACQUES REISSE
Faculté des Sciences Appliquées, Service de Chimie Organique E.P., Avenue F.-D. Roosevelt, 50, 1050 Bruxelles, Belgium

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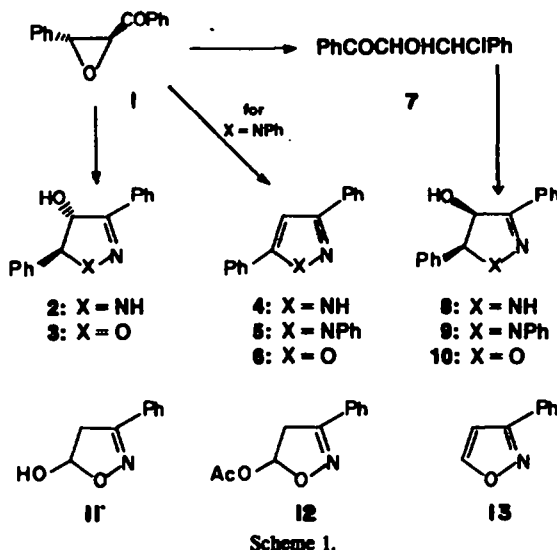
Abstract—The dehydration of various 4,5-dihydro-4- and -5-hydroxy derivatives of pyrazole and isoxazole has been investigated. Heats of dehydration of 4,5-dihydro-4-hydroxy-1,3,5-triphenylpyrazole and 4,5-dihydro-5-hydroxy-isoxazole are evaluated and used to assess the empirical resonance energy and conjugation energy of pyrazole and isoxazole. The former possesses resonance stabilisation comparable to pyrrole but that of the latter is low.

Quantitative assessments of aromaticity, or more precisely, of properties characteristic of aromatic compounds, provide a basis for rationalizing the chemistry of $4n+2\pi$ electron systems. The most comprehensive series of data, and arguably the most valuable, is furnished by evaluations of resonance energy, i.e. the enhanced stability of the aromatic system relative to a hypothetical nondelocalised structure or a model linear polyene.² Early resonance energy determinations were obtained from heats of combustion and hydrogenation data but in recent years the use of MO treatments has come to the fore.² In previous papers in this series new experimental approaches, which supplement the already available methods, have been described. Thus the resonance energy of the pyridone ring and related systems is well suited for evaluation by comparison of ΔH° for the heteroaromatic tautomeric equilibrium with the corresponding ΔH° for a saturated model,³ an approach applicable to a wider variety of systems than an earlier conceptually similar but more rigorous method based on gas phase isomerisations of analogous alkylated compounds.⁴ For 5-membered ring heterocycles, particularly pyrrole, indole and carbazole, resonance energy has been deduced from the reduced basicity of the ring relative to a nonaromatic model.^{5,6} Heteroaromatics which form pseudo bases stable in solution have been investigated on the basis of the hydroxylation equilibrium constants.^{1,6}

The present paper reports assessment of resonance energy utilising the heat of dehydration of a hydroxydihydro derivative of an aromatic compound. Although the approach should be general for a variety of systems, the comparative ease of preparation of 4,5-dihydro-4- and -5-hydroxy-isoxazoles and -pyrazoles prompted us to study initially members of these series, viz. 2, 3, 8–11.

RESULTS AND DISCUSSION

Preparation of compounds. *trans*-4,5-Dihydro-4-hydroxy-3,5-diphenylpyrazole 2 was prepared from



trans-chalcone epoxide 1 and hydrazine by the published route,⁷ however, the corresponding reactions of 1 with hydroxylamine in dioxan and in ethanol both gave 3, m.p. 172–174°, rather than substances of different melting points (m.p.s 193–194° and 172–173°) as reported elsewhere.⁸ The *trans* configuration for 3 was assigned on the basis of the low value for $J_{4,5} = 3$ Hz (CDCl_3 solution). Reaction of the *erythro* chlorohydrin 7, derived from 1, with hydrazine gave the *cis* derivative 8 as reported,⁷ but we found it was dehydrated during purification and we gave it no further attention. However, 7 with hydroxylamine and phenylhydrazine afforded the relatively stable novel *cis*-derivatives 9 and 10 ($J_{4,5} = 7.5$ and 9 Hz respectively). 4,5-Dihydro-5-hydroxy-3-phenylisoxazole 11,⁹ and the dehydrated and fully-conjugated systems also required for the study, viz. 4,⁷ 5,¹⁰ 6¹¹ and 13⁹ were prepared by literature routes.

Qualitative dehydration studies. UV Spectral data for the dihydrohydroxy compounds, 2, 3, 9, 10 and 11 in ethanol, and of the protonated forms of the aromatic systems 4–6, 13 in H_2SO_4 are reported in Table 1. The spectra of the cations were invariant over at least the first 20 min of preparation indicating the stability of the cations in the acid medium. The dehydrations of 2, 3, 9–11 in H_2SO_4 were followed by UV spectroscopy. No attempt was made to obtain rate data but from qualitative observations, Table 1, we conclude: (i) the isoxazole derivatives 3 and 10 dehydrate less readily than the corresponding pyrazoles 2, 8 (which dehydrated on recrystallisation) and 9, which is consistent with the expected differential stability of the O and N stabilised carbenium ion intermediate generated by loss of the OH group (as H_2O); (ii) in both the dihydro-4-hydroxy-isoxazole and -pyrazole series the *cis* isomers dehydrate more readily than the corresponding *trans* isomers reflecting the release of greater steric strain on carbenium ion formation in the *cis* series; (iii) the 5-hydroxy derivative 11 dehydrates much more readily than members of the 4-hydroxy series.

The feasibility of using acetic anhydride and phosphorus oxychloride as dehydration agents was investigated by measuring the UV spectra of 2 in these media. However the spectra were unchanged over 35 min from dissolution.

Quantitative dehydration studies. Of the five dihydrohydroxy compounds 2, 3, 9–11 only 9 and 11 were considered to dehydrate sufficiently fast to undertake calorimetric heat of dehydration measurements. Heat changes on dissolving the dihydrohydroxy derivatives [Arom HOH] and the corresponding aromatic compound [Arom] in H_2SO_4 , ΔH_A and ΔH_B respectively, are reported in Table 2. Scheme 2 defines the heat changes involved, some of which refer strictly to very highly biased equilibrium reactions, e.g. ΔH_4 and ΔH_5 . Both ΔH_A and ΔH_B are composite terms given by eqns (1) and (2).

$\dagger Q$ is of course a function of the solvent-solute interactions but is a function also of the solvent cohesive properties and of the size of the solute (cavity term) (J. J. Moura Ramos, M.-L. Stien and J. Reisse, *Chem. Phys. Letters* 42, 373 (1976)). This last contribution is probably very similar for [Arom] and [Arom OH] while the solvent-solute interaction may differ by 2 to 4 kcal/mole.

$$\Delta H_A = \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 \quad (1)$$

$$\Delta H_B = \Delta H_4 + \Delta H_9 \quad (2)$$

Now ΔH_1 , ΔH_4 and ΔH_8 are given by eqns (3–5) and combining these with eqns (1) and (2) gives eqn (6).

$$\Delta H_1 = \Delta H_3 + \Delta H_8 - \Delta H_6 \quad (3)$$

$$\Delta H_6 = \Delta H_7 - \Delta H_2 \quad (4)$$

$$\Delta H_8 = \Delta H_{10} - \Delta H_9 \quad (5)$$

$$\Delta H_1 = \Delta H_A - \Delta H_B + \Delta H_{10} - \Delta H_7 - \Delta H_5 \quad (6)$$

A value for ΔH_3 of -8.2 ± 0.3 kcal mole $^{-1}$ can be estimated from data reported elsewhere¹² and we elected to evaluate ΔH_7 and ΔH_{10} by measuring the heats of solution of [Arom HOH] and [Arom] in a nonpolar solvent. Essentially, this assumes the heat of dissolution ΔH_s is related to the heat of vapourisation/sublimation, ΔH_v , by $\Delta H_s = \Delta H_v + Q$ where Q is an enthalpy term which is similar for [Arom] and [Arom HOH]. $\dagger$ A number of nonpolar solvents were considered but low solubility precluded the use of those which mimic the gas phase most closely, e.g. saturated hydrocarbons, CS_2 and CCl_4 . Accordingly we were compelled to use the less than ideal solvent chloroform; heats of solution in this solvent are given in Table 2. From the experimental data we obtain values for ΔH_1 (the heat of dehydration as defined by Scheme 2) of -25 kcal mole $^{-1}$ for 9 and -4 kcal mole $^{-1}$ for 11. The major source of error in these values derives from the use of chloroform as an inert solvent and this is difficult to estimate. However since we require a difference term, i.e. $\Delta H_{10} - \Delta H_7$, systematic effects may partially cancel, i.e. $\Delta Q \sim 0$, and we believe values for ΔH_1 are reliable to within ± 3 kcal mole $^{-1}$.

"Resonance energy" evaluations. The classical and probably most quoted resonance energy, hereafter called empirical resonance energy ERE, generally has been derived by comparing heats of combustion or hydrogenation of aromatics with those of simple unsaturated models.² Similarly comparison of the ΔH_1 values with the corresponding value ΔH_{11} , for the dehydration of cyclopentanol, viz. -2 ± 0.5 kcal mole $^{-1}$ (from $\Delta H_f(\text{g})$ cyclopentanol -57.97 ± 0.31 ,¹³ $\Delta H_f(\text{g})$ cyclopentene

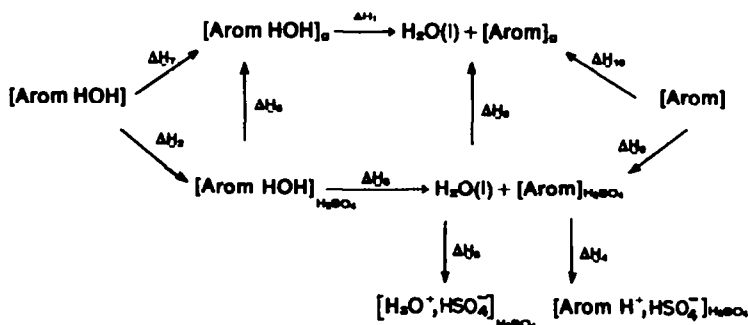
Table 1. UV spectral data

Compounds	EtOH		H_2SO_4		Comments
	λ_{max}	log ϵ	λ_{max}	log ϵ	
3,5-Diphenylpyrazole (4)	286	4.80	2.78	4.34	
<i>trans</i> -4,5-Dihydro-4-hydroxy derivative (2)	292	4.11			Incomplete dehydration (ca. 90%) after 75 min.
1,3,5-Triphenylpyrazole (5)	253	4.88	2.80	4.34	
<i>cis</i> -4,5-Dihydro-4-hydroxy derivative (9)	346	4.23			Dehydration complete within 10 min.
3,5-Diphenylisoxazole (6)	267	4.37	312	4.34	
<i>cis</i> -4,5-Dihydro-4-hydroxy derivative (10)	268	4.11	302	4.18	Spectrum unchanged in H_2SO_4 over 70 min.
<i>trans</i> -4,5-Dihydro-4-hydroxy derivative (3)	260	4.22	308	4.14	Spectrum unchanged in H_2SO_4 over 70 min.
3-Phenylisoxazole (13)	240	4.05	276	4.07	
4,5-Dihydro-5-hydroxy derivative (11)	266	4.61			Dehydration complete within 10 min.

Table 2. Calorimetric measurements at 25°

Compounds	Solvent	Heat of dissolution kcal mole ⁻¹	Remarks
9	H ₂ SO ₄	-47.65 ± 0.85	$\Delta\bar{H}_A$
8	H ₂ SO ₄	-16.43 ± 0.83	$\Delta\bar{H}_B$
9	CHCl ₃	4.98 ± 0.01	$\Delta\bar{H}_7$
5	CHCl ₃	3.29 ± 0.01	$\Delta\bar{H}_{10}$
11	H ₂ SO ₄	-22.72 ± 0.68	$\Delta\bar{H}_A$
13	H ₂ SO ₄	-15.47 ± 0.17	$\Delta\bar{H}_B$
11	CHCl ₃	3.98 ± 0.02	$\Delta\bar{H}_7$
13	CHCl ₃	-0.80 ± 0.01	$\Delta\bar{H}_{10}$

$$^a \Delta\bar{H}_5 = -8.2 \pm 0.3 \text{ kcal mole}^{-1}$$



Scheme 2.

+8.23 ± 0.22,¹⁴ and $\Delta\bar{H}_f(l)$ water -68.32 kcal mole⁻¹¹⁵ provides the basis of the ERE evaluations for pyrazole and isoxazole [eqn (7)].

$$\text{ERE} = -\Delta\bar{H}_1 + \Delta\bar{H}_{11} + R_1 - R_2 + R_3 \quad (7)$$

The other terms in eqn (7) are R_1 , the resonance inherent in the X-N=C fragment in [Arom HOH], R_2 , the resonance associated with conjugation of the ring with the C-5 phenyl group in [Arom], and R_3 , a term arising from differential conjugation of pendant phenyl groups (at the 1 and 3 positions) in [Arom HOH] and [Arom]. In calculating $\text{ERE}_{\text{pyrazole}}$ we assume R_1 (N=N=C) = 4 ± 1 kcal mole⁻¹ because it should be comparable to enamine resonance energy,¹⁶ R_2 = 2 ± 0.5 kcal mole⁻¹ from the difference in ERE of styrene and benzene,¹⁷ and R_3 = 0 ± 0.5, whence $\text{ERE}_{\text{pyrazole}}$ = 25 ± 6 kcal mole⁻¹. For isoxazole we take R_1 = 4 ± 1 kcal mole⁻¹ (cf. the ERE of ethyl vinyl ether 3.6 kcal mole⁻¹).¹⁷ R_2 is of course zero and R_3 , which now refers to only one pendant phenyl, we take as 0 ± 0.5 kcal mole⁻¹ whence $\text{ERE}_{\text{isoxazole}}$ = 6 ± 5 kcal mole⁻¹.

Previous values for $\text{ERE}_{\text{pyrazole}}$ have fallen in the range 26.8–41.5 kcal mole⁻¹.² What appears to be the only measurement of $\text{ERE}_{\text{isoxazole}}$ provided values for various methyl isoxazoles of 50 kcal mole⁻¹¹⁸ which would seem to be far too high.¹⁹ The very low value obtained here is consistent with an MO calculation which assigned isoxazole a delocalisation energy of only 6% that of benzene.²⁰

Conjugation energies. The hybridisation of the ring atoms bonded to the carbon atoms involved in the dehydration reaction are not the same in the heterocyclic system and the alicyclic model. This aspect of ERE evaluations has been discussed in depth by Dewar and Schmeising²¹ who contended that single bond energies vary significantly with the hybridisation of the carbon atoms. Subsequently Cox^{22,23} summarised appropriate

data and deduced a bond energy scheme which takes into account these variations. Using Cox's bond contributions to molecular heats of formation²³ and the value for $\Delta\bar{H}_f(l)$ for water we obtain "calculated" values for $\Delta\bar{H}_1$ (Schemes 3 and 4). The difference between the experimental and calculated values gives the *conjugation energy*, a term not to be confused with ERE.²³ Assuming the conjugation between pendant phenyl groups and the X-N=C fragment is the same in [Arom HOH] and [Arom], the *conjugation energies* for pyrazole (bonded to a 5-phenyl substituent) and isoxazole are 14 and 1 kcal mole⁻¹ respectively.

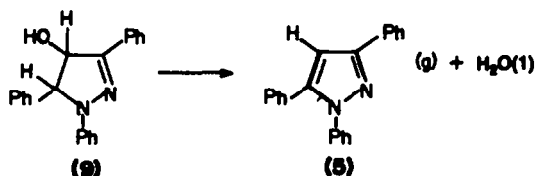
Conjugation energies have been calculated previously for pyrazole, 27 kcal mole⁻¹, but not for isoxazole.²³ The value for pyrazole however was considered uncertain because of the choice of the bond energy for the N-N bond, a term which fortunately cancels in the present calculation. Our value of 14 kcal mole⁻¹ lies close to pyrrole, 15 kcal mole⁻¹, and less than benzene, 22 kcal mole⁻¹.²³ The isoxazole conjugation energy is rather less than that for furan, 8 kcal mole⁻¹,²³ but close to 5% of that for benzene (cf. the delocalisation energies referred to above).²⁰

CONCLUSION

Calorimetric determinations of the heat of dehydration provide a feasible alternative for evaluating resonance energies of aromatic systems, providing dehydration proceeds readily. ERE and *conjugation energies* obtained for pyrazole and isoxazole show that pyrazole and pyrrole share comparable resonance stabilisation but isoxazole is very much less aromatic.

EXPERIMENTAL

Spectral measurements. UV spectra were measured using a Unicam SP 500 spectrophotometer and NMR obtained using a Perkin Elmer R 12 spectrometer operating at 60 MHz.



$\text{Csp}^3 - \text{OH}$	-45.3 kcal mole ⁻¹	$\text{Csp}^2 - \text{Csp}^2$	-12.5 kcal mole ⁻¹
$(\text{Csp}^3 - \text{H})^1$	- 1.7 " "	$\text{Csp}^2 - \text{Ph}^*$	-12.5 " "
$(\text{Csp}^3 - \text{H})_{\text{O}}^1$	+ 0.4 " "	$\text{C} = \text{C}$	+37.9 " "
$\text{Csp}^3 - \text{N}$	+ 8.2 " "	$\text{Csp}^2 - \text{N}$	+ 4.0 " "
$\text{Csp}^3 - \text{Csp}^2$	- 4.1 " "	$(\text{Csp}^2 - \text{H})^1$	- 5.6 " "
$\text{Csp}^3 - \text{Csp}^3$	+ 0.4 " "	$\Delta H_f^\circ \text{H}_2\text{O(l)}$	-68.3 " "
$\text{Csp}^3 - \text{Ph}^*$	- 4.1 " "	Total	-57.0 " "
Total	-46.2 " "		

Calculated $\Delta H_1 = -10.8 \text{ kcal mole}^{-1}$

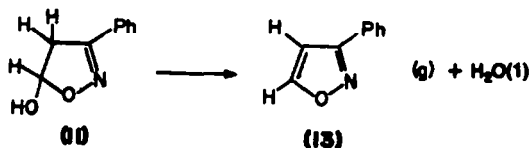
^a Superscript 1 refers to a primary C-H bond.

Subscript _O refers to a C-H bond adjacent to an O atom.

* bond contributions to ΔH_f° for C-Ph bonds were taken to be equal to those for C - Csp^2 bonds, as no values were given for C-Ph bonds.

Any small error here would probably occur in both totals and so cancel out.

Scheme 3. Bond energy scheme for the dehydration of (9)^a.



$\text{Csp}^3 - \text{OH}$	-45.3 kcal mole ⁻¹	$\text{Csp}^2 - \text{Csp}^2$	-12.5 kcal mole ⁻¹
$2(\text{Csp}^3 - \text{H})''$	- 5.2 " "	$\text{C} = \text{C}$	+37.9 " "
$(\text{Csp}^3 - \text{H})_{\text{OO}}^1$	+ 2.0 " "	$(\text{Csp}^2 - \text{H})^1$	- 5.6 " "
$\text{Csp}^3 - \text{O}$	-19.2 " "	$(\text{Csp}^2 - \text{H})_{\text{O}}^1$	- 4.4 " "
$\text{Csp}^3 - \text{Csp}^3$	+ 0.4 " "	$\text{Csp}^3 - \text{O}$	-21.4 " "
$\text{Csp}^3 - \text{Csp}^2$	- 4.1 " "	$\Delta H_f^\circ \text{H}_2\text{O(l)}$	-68.3 " "
Total	-71.4 " "	Total	-74.3 " "

^a. Calculated $\Delta H_1 = -2.9 \text{ kcal mole}^{-1}$

^a Superscript '' refers to a secondary C-H bond.

Subscript _{OO} refers to a C-H bond adjacent to two O atoms. The value for this bond contribution to ΔH_f° (g) was estimated from the values for $(\text{Csp}^3 - \text{H})^1$ and $(\text{Csp}^3 - \text{H})_{\text{O}}^1$.

superscript 1 and subscript _O - see notes to Scheme 3.

Scheme 4. Bond energy scheme for the dehydration of (11)^a.

Compounds. The following materials were prepared using literature routes: *trans* - 4,5 - dihydro - 4 - hydroxy - 3,5 - diphenylpyrazole⁷ 2, m.p. 210-211° (lit.⁷ m.p. 209°); *trans* - 4,5 - dihydro - 4 - hydroxy - 3,5 - diphenylisoxazole⁸ 3, m.p. 172-174° (lit.⁸ m.p. 172-173°); *cis* - 4,5 - dihydro - 5 - hydroxy - 3,5 - diphenylpyrazole⁷ 8, m.p. 160°, decomposed to 4 during purification, (lit.⁷ m.p. 172-173°); 4,5 - dihydro - 5 - hydroxy - 3 - phenylisoxazole⁹ 11, m.p. 120.5-121.5° (lit.⁹ m.p. 120-122°); *trans* - chalcone epoxide⁸ 1, m.p. 89-90° (lit.⁸ m.p. 89-90°); *erythro* - 1 -

chloro - 2 - hydroxy - 1,3 - diphenylpropan - 3 - one¹⁰ 7, m.p. 105-110° (lit.¹⁰ m.p. 106-107°); 3,5-diphenylpyrazole⁷ 4, m.p. 203-205° (lit.⁷ m.p. 198-199°); 1,3,5-triphenylpyrazole¹⁰ 5, m.p. 141.5-142° (lit.¹⁰ m.p. 138-138.5°); 3,5-diphenylisoxazole¹¹ 6, m.p. 141-143° (lit.¹¹ m.p. 141°); 3-phenylisoxazole⁹ 13, b.p. 126-128°/15 mm (lit.⁹ 124°/12 mm).

cis - 4,5 - Dihydro - 4 - hydroxy - 1,3,5 - triphenylpyrazole 9. *erythro* - 1 - Chloro - 2 - hydroxy - 1,3 - diphenyl - 3 - propanone (2.60 g, 0.01 mole) in ethanol (30 ml) and phenylhydrazine (2.16 g,

0.02 mole) were heated to reflux for 8 min and allowed to cool. A mixture of colourless needles (m.p. 180–190°) and colourless flakes (decomposing at 170–200°): $\nu_{\max}$ (Nujol) 3210, 1590, 1495, 890 and 765 cm^{-1} ; $\tau[(\text{CD}_3)_2\text{CO}]$ 2.5–3.3(m), formed, the larger proportion being the needles. Recrystallisation from ethanol afforded solely the needles (m.p. 184–191°). Removal of solvent from the mother liquor gave colourless needles of a different compound whose m.p. and IR spectra were identical with those of 1,3,5-triphenylpyrazole. Further recrystallisation of the needles (m.p. 184–191°) afforded pure *cis*-4,5-dihydro-4-hydroxy-1,3,5-triphenylpyrazole (1.5 g, 48%), m.p. 196–196.5° (Found: C, 79.9; H, 5.8; N, 8.9. $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}$ requires: C, 80.2; H, 5.8; N, 8.9%). $\nu_{\max}$ (Nujol) 3540 (OH), 1590, 1495, 1320, 1130, 1080, 740 and 690 cm^{-1} ; τ ($\text{CF}_3\text{CO}_2\text{H}$) 2.0–3.0(m); τ (acetone- D_6) 1.9–3.5 (15 H, m, Ph), 4.6 (1H, half of an AB quartet after shaking with D_2O , J 9 Hz, H-4), 4.9 (1H, half of an AB quartet, J 4 Hz, H-5) and 5.8 (1H, d, J 8 Hz, disappears on shaking with D_2O , OH).

cis-4,5-Dihydro-4-hydroxy-3,5-diphenylisoxazole (10), *erythro*-1-Chloro-2-hydroxy-1,3-diphenyl-3-propanone (2.60 g, 0.01 mole) in ethanol (20 ml) and hydroxylammonium chloride (2 g) in water (6 ml) were heated to reflux for 5 min and allowed to cool. Colourless flakes formed (m.p. 171–176° with some melting at ca. 140° indicating the probable presence of a little 3,5-diphenylisoxazole). Recrystallisation twice from ethanol (10 ml) gave pure *cis*-4,5-dihydro-4-hydroxy-3,5-diphenylisoxazole (1.4 g, 59%), m.p. 180–181° (Found: C, 75.0; H, 5.6; N, 6.2. $\text{C}_{15}\text{H}_{11}\text{NO}_2$ requires: C, 75.3; H, 5.5; N, 5.9%). $\nu_{\max}$ (Nujol) 3400 (OH), 1580, 1495, 1105, 890, 735, 700 and 685 cm^{-1} ; τ ($(\text{CD}_3)_2\text{SO}$) 2.0–3.2 (10H, m, Ph), 4.50 (2H, AB quartet, J 7.5 Hz, H-4 & H-5) and 5.20 (1H, disappears on shaking with D_2O , OH).

Calorimetric measurements. These measurements were performed either with an LKB 8700 calorimeter (solvent H_2SO_4) or with the calorimeter described previously;²⁴ in both cases the performance of the calorimeter was checked by measurement of the heat of solution of tris(hydroxymethyl)aminomethane in aqueous hydrochloric acid.²⁵ Thermochemical functions are expressed in terms of the defined calorie (4.1840 J) and refer to the isothermal process at 25°. Measurements were carried out with solutes such that their concentration in the final solution was about 3×10^{-3} mole l^{-1} ; this is sufficiently dilute to consider that the heats of solution refer to infinite dilution.

The solution process in solvent chloroform took place rapidly and measurements of heats of solution in this solvent were very reproducible (Table 2). Since chloroform has an appreciable vapour pressure at 25°, there is a correction to be made for the evaporation of the solvent into the vapour space of the ampoule. Separate experiments established that this ampoule breaking correction was 0.1374 cal; all heats of solution in chloroform have been corrected.

The solution process in solvent sulphuric acid was less straightforward, because of slow (and possibly not quite complete) dissolution: thus the relatively large quoted errors in these cases, even though the calorimetric system is inherently capable of more accurate or reproducible results.

REFERENCES

- ¹Part VI see M. J. Cook, A. R. Katritzky, A. D. Page, R. D. Tack and H. Witke, *Tetrahedron* **32**, 1773 (1976).
- ²For a review see M. J. Cook, A. R. Katritzky and P. Linda, *Adv. Heterocycl. Chem.* **17**, 255 (1974).
- ³M. J. Cook, A. R. Katritzky, P. Linda and R. D. Tack, *Chem. Comm.* 510 (1971); *J. Chem. Soc. Perkin II* 1295 (1972); *Ibid.* 1080 (1973).
- ⁴P. Beak, J. Bonham and J. T. Lee, *J. Am. Chem. Soc.* **90**, 1569 (1968).
- ⁵M. P. Carmody, M. J. Cook, N. L. Dassanayake, A. R. Katritzky, P. Linda and R. D. Tack, *Tetrahedron* **32**, 1767 (1976); see also D. Lloyd and D. R. Marshall, *Chem. Ind. (London)* 335 (1972).
- ⁶M. J. Cook, A. R. Katritzky, P. Linda and R. D. Tack, *Tetrahedron Letters* 5019 (1972).
- ⁷G. Litkei, A. Neubauer and R. Bognar, *Tetrahedron* **28**, 3241 (1972).
- ⁸H. J. Roth and M. Schwarz, *Arch. Pharm.* **294**, 478 (1961); **294**, 769 (1961).
- ⁹R. G. Micetich, *Can. J. Chem.* **48**, 467 (1970).
- ¹⁰O. Widman, *Chem. Ber.* **49**, 477 (1916).
- ¹¹K. S. R. Krishna Mohan Rao and N. V. Subba Rao, *Indian J. Chem.* **6**, 66 (1968).
- ¹²K. Lauer and R. Oda, *Chem. Ber.* **70**, 333 (1937).
- ¹³J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, p. 206. Academic Press, London (1970).
- ¹⁴Ref. 13, p. 144.
- ¹⁵F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffé, *Selected Values of Chemical Thermodynamic Properties Part 1 Tables*, p. 9. National Bureau of Standards, Circular 500, U.S. Government Printing Office, Washington, D.C. (1952).
- ¹⁶Derived using the results of F. W. Fowler, personal communication, and discussed in detail in Ref. 1.
- ¹⁷G. W. Wheland, *Resonance in Organic Chemistry*, p. 132. Wiley, New York (1955).
- ¹⁸G. Tappi, *Gazz. Chim. Ital.* **70**, 414 (1940) [*Chem. Abstr.* **36**, 6404^e (1942)].
- ¹⁹M. L. Casey, D. S. Kemp, K. G. Paul and D. D. Cox, *J. Org. Chem.* **38**, 2294 (1973).
- ²⁰G. Del Re, in *Aromaticity, Pseudoaromaticity, Anti Aromaticity* (Edited by E. D. Bergmann and B. Pullman), (Proceedings, Jerusalem Symp. Quant. Chem. Biochem. 1970 Vol. III), p. 74. Academic Press, New York (1971).
- ²¹M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **5**, 166 (1959); **11**, 96 (1960).
- ²²J. D. Cox, *Ibid.* **18**, 1337 (1962).
- ²³J. D. Cox, *Ibid.* **19**, 1175 (1963).
- ²⁴M. H. Abraham, R. J. Irving and G. F. Johnston, *J. Chem. Soc. (A)* 199 (1970).
- ²⁵J. O. Hill, G. Ojelund and I. Wadsö, *J. Chem. Thermodyn.* **1**, 111 (1969) [*Chem. Abstr.* **71**, 54351z (1969)].