

# DISTINCTION OF 3-(N,N-DIMETHYLAMINO)COUMARIN FROM HYPOTHETIC 2-(N,N-DIMETHYLAMINO)-1,3-INDANEDIONE BY INFRARED SPECTROSCOPY

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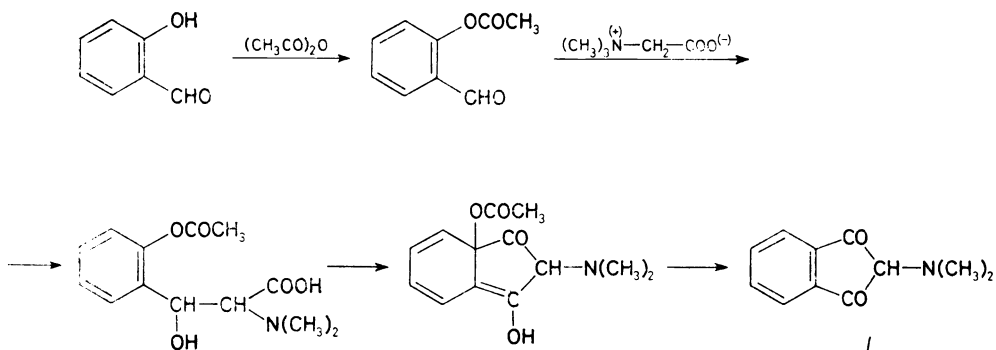
Received March 29, 1989

Accepted June 6, 1989

*Dedicated to Professor Otto Exner on the occasion of his 65th birthday.*

A detailed investigation of infrared spectra was used to distinguish the structure of 3-(N,N-dimethylamino)coumarin from the structure of hypothetical 2-(N,N-dimethylamino)-1,3-indanedione suggested earlier as the product of the reaction between salicylaldehyde, acetanhydride and betaine.

In 1981 Masaaki<sup>1</sup> claimed 2-(N,N-dimethylamino)-1,3-indanedione (*I*) as an efficient absorber of UV radiation and described its preparation as a new type of reaction between salicylaldehyde, acetanhydride and betaine (Scheme 1). The newly prepared

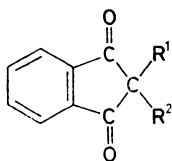


SCHEME 1

compound was characterized by melting point, elemental analysis, UV, IR, <sup>1</sup>H NMR and mass spectroscopy. The cyclic 1,3-dicarbonyl structure was concluded from the

existence of intensive  $\nu(\text{C}=\text{O})$  band at  $1\,705\text{ cm}^{-1}$  (in KBr), while from  $^1\text{H NMR}$  spectra resulted only the structure of the *ortho* substituted benzene ring and N,N-dimethylamino group. In mass spectra merely the base peak was assigned to the molecular ion.

As the formation of 2-(N,N-dimethylamino)-1,3-indanedione (*I*) by described reaction (Scheme 1) because of discrepancies found in (ref.<sup>2</sup>) seemed rather unlikely, we decided to reproduce the above reaction. We found the same crystalline substance with reported melting point, correct elemental analysis and the same spectral properties as Masaaki<sup>1</sup>. In order to elucidate the correct structure we examined in detail the isolated compound by IR spectroscopy. The IR spectra of compound were measured in solvents of different polarity and associational ability and compared



- II,  $\text{R}^1 = \text{N}(\text{CH}_3)_2$ ;  $\text{R}^2 = \text{CH}_3$   
 III,  $\text{R}^1 = \text{N}(\text{CH}_3)_2$ ;  $\text{R}^2 = \text{C}_6\text{H}_5$   
 IV,  $\text{R}^1 = \text{H}$ ;  $\text{R}^2 = \text{CH}_3$   
 V,  $\text{R}^1 = \text{H}$ ;  $\text{R}^2 = \text{C}_6\text{H}_5$

with those of analogous derivatives of 2-(N,N-dimethylamino)-1,3-indanedione (*II* and *III*) (prepared in different way than given in Scheme 1) and with spectra of other 1,3-indanediones (*IV* and *V*). To make complete the informations about the structure, the  $^{13}\text{C NMR}$  data (measured in  $\text{CDCl}_3$ ) were used too.

## EXPERIMENTAL

The compound of supposed structure *I* was prepared by described procedure<sup>1</sup>. Derivatives of 1,3-indanediones were synthesized according to<sup>3-5</sup>.

The IR spectra were taken in the region of  $1\,800\text{--}1\,600\text{ cm}^{-1}$  on a Perkin-Elmer 180 grating spectrophotometer at the room temperature. For measurements solutions in heptane, tetrachloromethane, benzene, hexamethylphosphoramide, 1,2-dichloroethane, acetonitrile, trichloromethane, methanol and NaCl cells 0.1, 1.0 and 10 mm in thickness were used. The concentration of measured solutions were chosen to reach transmittance between 25% to 30%. The calibration of wave number scale of the instrument was checked using standard spectra of polystyrene and water vapour. Peak positions were determined from three measurements with the accuracy of  $\pm 0.1\text{ cm}^{-1}$ . The intensity ratios (*R*) were calculated from values of  $\epsilon_{\text{max}}$  determined by method of base line. The IR spectra of some compounds were also measured in the region of  $4\,000\text{--}700\text{ cm}^{-1}$  in paraffin oil, tetrachloro- and trichloromethane using KBr cells of 0.02 mm and 0.1 mm thickness, respectively.

## RESULTS AND DISCUSSION

The IR spectral data of compound assigned by Masaaki<sup>1</sup> to 2-(N,N-dimethylamino)-1,3-indanedione (*I*) are given in Table I and the analogical data for some 1,3-indanedione derivatives (*II–V*) are listed in Tables II and III. The compound of assumed structure *I* exhibit in the region of C=O stretching vibrations a doublet with a more intense lower frequency band ( $\nu_1(\text{C=O})$ ) and a less intense higher frequency band ( $\nu_2(\text{C=O})$ ). This behaviour at first sight is indeed similar to that of 1,3-indanedione derivatives<sup>6</sup> (e.g. compounds *II–V*, Tables II and III), the maxima of which can be assigned to antisymmetric ( $\nu_{\text{as}}(\text{C=O})$ ) and symmetric ( $\nu_{\text{s}}(\text{C=O})$ ) vibrations of mechanically coupled cyclic 1,3-dicarbonyl system. However, a more detailed investigation of IR data in 1 800–1 700  $\text{cm}^{-1}$  region shows a substantial difference between 1,3-indanediones and this compound. In the case of compound of supposed structure *I* the frequency separation  $\Delta\nu(\text{C=O}) = \nu_2(\text{C=O}) - \nu_1(\text{C=O})$  of carbonyl doublet significantly depends on the type of solvent used. In aprotic non-polar solvent (e.g. heptane) the lowest value,  $\Delta\tilde{\nu}(\text{C=O}) = 14.5 \text{ cm}^{-1}$ , can be observed. Raising the polarity and associational ability of solvent the carbonyl frequency separation gradually increases, and in methanol reach a value  $\Delta\tilde{\nu}(\text{C=O}) = 46.0 \text{ cm}^{-1}$ . On the other hand, all similar 1,3-indanediones (*II–V*) exhibit by variation of solvent only a very little change in the frequency separation of analogous doublet:  $\Delta\tilde{\nu}(\text{C=O}) = 1–6 \text{ cm}^{-1}$ . It follows from the above results that in the case of compounds of assumed structure *I* the carbonyl stretching frequency doublet will not be probably caused by the vibrational coupling in cyclic 1,3-dicarbonyl system. A different behaviour of this compound from 1,3-indanediones (*II–V*) can be also observed by examination of intensity ratio *R* of both maxima of the  $\nu(\text{C=O})$  doublet.

TABLE I

Infrared spectral data ( $\tilde{\nu}$ ,  $\text{cm}^{-1}$ ) of compound assigned by Masaaki<sup>1</sup> to structure *I*

Solvent	$\nu_1(\text{C=O})$	$\nu_2(\text{C=O})$	$\Delta\nu(\text{C=O})$	$R^a$
$\text{C}_7\text{H}_{16}$	1 739.5	1 754.0	14.5	0.43
$\text{CCl}_4$	1 731.3	1 754.3	23.0	0.43
$\text{C}_6\text{H}_6$	1 728.3	1 753.3	25.0	0.58
HMPTA <sup>b</sup>	1 724.3	1 753.3	29.0	0.17
$\text{ClCH}_2\text{CH}_2\text{Cl}$	1 722.3	1 755.8	33.5	0.20
$\text{CH}_3\text{CN}$	1 722.8	1 758.8	36.0	0.20
$\text{CHCl}_3$	1 714.8	1 756.3	41.5	0.22
$\text{CH}_3\text{OH}$	1 709.0 <sup>c</sup>	1 755.0	46.0	0.25

<sup>a</sup> Intensity ratio of the absorption bands  $\nu_2(\text{C=O}) : \nu_1(\text{C=O})$ ; <sup>b</sup> hexamethylphosphortriamide;

<sup>c</sup> additional band of low intensity at  $\tilde{\nu} = 1 723.3 \text{ cm}^{-1}$ .

TABLE II  
Infrared spectral data ( $\tilde{\nu}$ ,  $\text{cm}^{-1}$ ) for 2-(N,N-dimethylamino)-2-methyl- (II) and 2-(N,N-dimethylamino)-2-phenyl-1,3-indanedione (III)

Solvent	II				III			
	$\nu_{\text{as}}(\text{C}=\text{O})$	$\nu_{\text{s}}(\text{C}=\text{O})$	$\Delta\nu(\text{C}=\text{O})$	$R^a$	$\nu_{\text{as}}(\text{C}=\text{O})$	$\nu_{\text{s}}(\text{C}=\text{O})$	$\Delta\nu(\text{C}=\text{O})$	$R^a$
$\text{C}_7\text{H}_{16}$	1 716.3	1 751.8	35.5	0.61	1 708.3	1 746.8	38.5	0.57
$\text{CCl}_4$	1 713.5	1 749.8	36.3	0.50	1 706.3	1 745.3	39.0	0.63
$\text{C}_6\text{H}_6$	1 712.1	1 748.1	36.0	0.52	1 704.8	1 743.8	39.0	0.60
HMPA <sup>b</sup>	1 709.8	1 745.3	35.5	0.60	1 703.3	1 742.3	39.0	0.68
$\text{ClCH}_2\text{CH}_2\text{Cl}$	1 710.3	1 746.8	36.5	0.62	1 703.6	1 742.6	39.0	0.53
$\text{CH}_3\text{CN}$	1 710.3	1 747.0	36.7	0.62	1 704.3	1 743.3	39.0	0.68
$\text{CHCl}_3$	1 710.3	1 746.8	36.5	0.54	1 703.6	1 742.8	39.2	0.56
$\text{CH}_3\text{OH}$	1 710.3	1 747.0	36.7	0.53	1 704.3	1 743.3	39.0	0.68

<sup>a,b</sup> See Table I.

TABLE III  
Infrared spectral data ( $\bar{\nu}$ ,  $\text{cm}^{-1}$ ) for 2-methyl- (IV) and 2-phenyl-1,3-indanedione (V)

Solvent	IV				V			
	$\nu_{\text{as}}(\text{C}=\text{O})$	$\nu_{\text{s}}(\text{C}=\text{O})$	$\Delta\nu(\text{C}=\text{O})$	$R^a$	$\nu_{\text{as}}(\text{C}=\text{O})$	$\nu_{\text{s}}(\text{C}=\text{O})$	$\Delta\nu(\text{C}=\text{O})$	$R^a$
$\text{C}_7\text{H}_{16}$	1 721.3	1 755.8	34.5	0.42	1 723.8	1 754.3	30.5	0.47
$\text{CCl}_4$	1 716.9	1 752.8	35.9	0.32	1 720.0	1 751.0	31.0	0.40
$\text{C}_6\text{H}_6$	1 715.8	1 751.3	35.5	0.45	1 718.6	1 750.0	31.4	0.41
HMPTA <sup>b</sup>	1 712.8	1 747.3	34.5	0.33	1 712.8	1 747.8	35.0	0.41
$\text{ClCH}_2\text{CH}_2\text{Cl}$	1 713.7	1 749.8	36.1	0.36	1 715.8	1 749.3	33.5	0.35
$\text{CH}_3\text{CN}$	1 714.3	1 749.8	35.5	0.43	1 715.6	1 749.6	34.0	0.34
$\text{CHCl}_3$	1 712.1	1 749.0	36.9	0.32	1 714.8	1 748.8	34.0	0.48
$\text{CH}_3\text{OH}$	1 712.8	1 749.9	37.1	0.37	1 713.8	1 749.3	35.5	0.49

<sup>a,b</sup> See Table I.

As follows from the Table I, the ratio  $R$  of investigated compound markedly decreases as the polarity and associational ability of solvent increases, while in the case of 1,3-indanedione derivatives (see Tables II and III) the value of  $R$  does practically not change with properties of solvent. The comparison of Figs 1 and 2 conclusively illustrates a marked difference between the spectral behaviour of compound with assumed structure *I* and 2-(*N,N*-dimethylamino)-2-methyl-1,3-indanedione (*II*) in solvent mixtures. It is evident from the Fig. 1, that both the shape of spectrum and the intensity ratio of bands does clearly change as the portion of polar component in solvent mixture increases. In contrary, for compounds *II* (Fig. 2), like in the case of other 1,3-indanedione derivatives, both maxima of the  $\nu(\text{C}=\text{O})$  doublet are regularly shifted to lower frequencies as the polarity of mixture increases, whereby their intensity ratio remains practically the same.

Comparing the  $\nu_1(\text{C}=\text{O})$  value (in  $\text{CCl}_4$ ) for compound of supposed structure *I* with corresponding value of  $\nu_{\text{as}}(\text{C}=\text{O})$   $1720.7\text{ cm}^{-1}$  for 1,3-indanedione, it can be ascertain that the introduction of dimethylamino group in the position 2 of 1,3-indanedione skeleton involves an increase in frequency by  $10.6\text{ cm}^{-1}$ , which is however in a sharp contradiction with strong electron-donating properties of  $\text{N}(\text{CH}_3)_2$  substituent. On the other hand, the comparison of  $\nu_{\text{as}}(\text{C}=\text{O})$  values (in  $\text{CCl}_4$ ) for couples of compounds *II*, *IV* and *III*, *V* (Tables II and III) shows quite an opposite result (i.e. a frequency decrease), which is in a good agreement with electron-donating effect of  $\text{N}(\text{CH}_3)_2$  group.

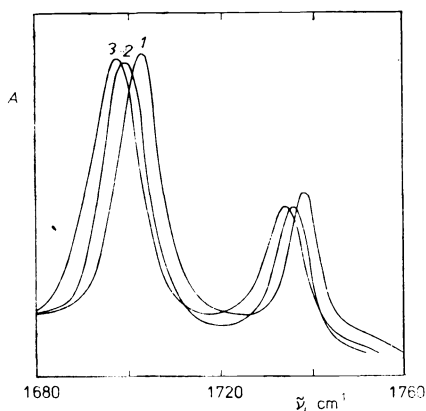


FIG. 1

Infrared spectra of compound assigned by Masaaki<sup>1</sup> to structure *I* in mixtures of heptane: trichloromethane 1 1 : 0; 2 1 : 1; 3 0 : 1

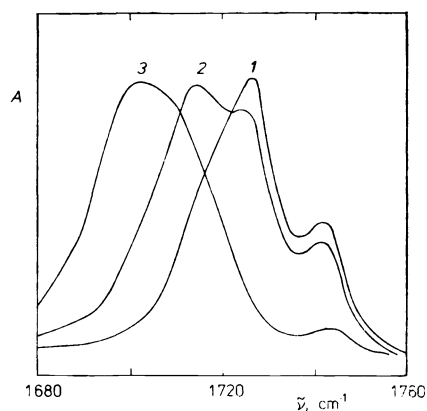


FIG. 2

Infrared spectra of 2-(*N,N*-dimethylamino)-2-methyl-1,3-indanedione (*II*) in mixture of heptane : trichloromethane 1 1 : 0; 2 7 : 3; 3 0 : 1

Earlier<sup>6,7</sup> a generally valid empirical relationship (Eq. (I)) was found between the  $\nu_s(\text{C=O})$  and  $\nu_{as}(\text{C=O})$  values of a great variety of 1,3-indanedione derivatives.

$$\nu_s(\text{C=O}) = 0.781 \cdot \nu_{as}(\text{C=O}) + 412.8 \quad (I)$$

The fitness of the above correlation in the most cases is better than  $\Delta\tilde{\nu} = \pm 3 \text{ cm}^{-1}$ , where  $\Delta\tilde{\nu} = \tilde{\nu}_{\text{exp.}} - \tilde{\nu}_{\text{calc.}}$  is a difference between the experimental and calculated frequency. Trying however to apply Eq. (I) to the values of  $\nu_1(\text{C=O})$  or  $\nu_2(\text{C=O})$  (in  $\text{CCl}_4$ ) for compounds of assumed structures *I* we observed significant deviations  $\Delta\tilde{\nu} = +14 \text{ cm}^{-1}$  and  $-17 \text{ cm}^{-1}$ . It follows from this and also from preceding experimental results that the origin of the splitting of  $\nu(\text{C=O})$  bands in mentioned compounds cannot be explained as a vibrational coupling in cyclic 1,3-dicarbonyl system.

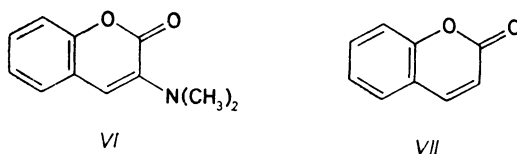
Another possibility to make clear this splitting is to consider Fermi resonance. The compound capable for Fermi resonance<sup>8</sup> and having a structure isomeric to *I* is 3-(N,N-dimethylamino) coumarin (*VI*). The rise of this compound by the reaction between salicylaldehyde, acetanhydride and betaine can be also easily explained<sup>2</sup> on the basis of existing classical conceptions. The infrared spectra of compound with supposed structure *I* conspicuously resemble the spectra of coumarin (*VII*) in whole region of  $4000 \text{ cm}^{-1}$  to  $700 \text{ cm}^{-1}$ . This allows us to assume, that the compound prepared by Masaaki<sup>1</sup> has a structure *VI*. The further comparison of some spectral properties for compounds *I* and *VII* is evident from Table IV. The frequency separation of carbonyl doublet in both compounds increases by  $\Delta\tilde{\nu}(\text{C=O}) = 12.0 - 18.5 \text{ cm}^{-1}$  passing from  $\text{CCl}_4$  to  $\text{CHCl}_3$  while the intensity ratio *R* of both maxima exhibit a significant decrease. These phenomena can be regarded<sup>8,9</sup> as a typical symptom of Fermi resonance. The data in Table IV show that the introduction of dimethylamino group in the position 3 of coumarin skeleton (structure *VI*

TABLE IV

Comparison of infrared spectral data for compound assigned by Masaaki<sup>1</sup> to structure *I* with those of coumarin (*VII*) ref.<sup>8</sup>

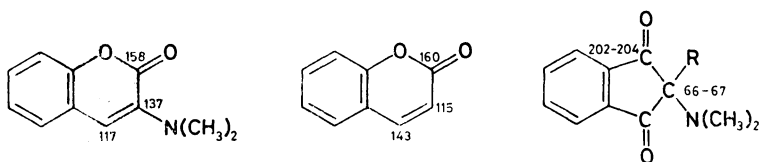
Compound	Solvent	$\tilde{\nu}, \text{cm}^{-1}$			<i>R</i> <sup>a</sup>
		$\nu_1(\text{C=O})$	$\nu_2(\text{C=O})$	$\Delta\nu(\text{C=O})$	
<i>I</i> ( <i>VI</i> )	$\text{CCl}_4$	1 731.3	1 754.3	23.0	0.43
	$\text{CHCl}_3$	1 714.8	1 756.3	41.5	0.22
<i>VII</i>	$\text{CCl}_4$	1 743.0	1 757.0	14.0	0.85
	$\text{CHCl}_3$	1 731.0	1 757.0	26.0	0.27

<sup>a</sup> See Table I.



suggested by us) causes a decrease in  $\nu_1(\text{C}=\text{O})$  value by  $11.7\text{ cm}^{-1}$  and  $26.2\text{ cm}^{-1}$  in  $\text{CCl}_4$  and  $\text{CHCl}_3$  respectively, which is in a fair agreement with electron-donating effect of  $\text{N}(\text{CH}_3)_2$  group.

The close similarity between the structure of investigated compound *I* and structure of coumarin (*VII*) as well as an expressive difference between the structure of this compound and structure of 2-substituted 2-(*N,N*-dimethylamino)-1,3-indanediones (*II* and *III*) shows also the comparison of  $^{13}\text{C}$  NMR chemical shifts (measured in  $\text{CDCl}_3$ , taken from<sup>10,11</sup>) in Scheme 2.



SCHEME 2

It can be confirmed on the basis of above results and discussion in (ref.<sup>2</sup>) that the product of the reaction between salicylaldehyde, acetanhydride and betaine described by Masaaki<sup>1</sup> is not 2-(*N,N*-dimethylamino)-1,3-indanedione (*I*), but isomeric 3-(*N,N*-dimethylamino)coumarin (*VI*).

The technical assistance of Mrs R. Vogrinčičová and † A. Paštrnáková from Institute of Chemistry, Comenius University, Bratislava is gratefully acknowledged.

## REFERENCES

1. Masaaki I.: Eur. Pat. Appl. 22, 647 (19181).
2. Hrnčiar P., Gáplovský A., Donovalová J.: Tetrahedron Lett. 1989, 1079.
3. Wanag G., Walbe U.: Chem. Ber. 71, 1448 (1938).
4. Wislicenus W.: Chem. Ber. 20, 593 (1887).
5. Michael A., Gabriel S.: Chem. Ber. 10, 391 (1877).
6. Perjéssy A., Hrnčiar P.: Tetrahedron 27, 6159 (1971).
7. Perjéssy A., Temkovitz P., Hrnčiar P.: Collect. Czech. Chem. Commun. 41, 2904 (1976).
8. Jones R. N., Angle C. L., Ito T., Smith R. J. D.: Can. J. Chem. 37, 2007 (1959).
9. Ortiz E., Fernandez Bertran J., Ballester L.: Spectrochim. Acta A 27, 1713 (1971).
10. Solčániová E.: Unpublished results.
11. Cussans N. J., Huckerby T. N.: Tetrahedron 31, 2719 (1975).

Translated by the author (A. P.).