APPLICATION OF IR SPECTROSCPY IN THE STRUCTURAL ANALYSIS OF RING AND CHAIN ISOMERS OF γ-KETO AMIDES

R. É. Valter and S. P. Valter

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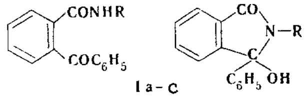
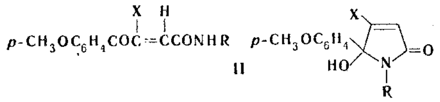
Recently there appeared a paper by Bhatt et al. [1], who, as a result of an erroneous interpretation of the IR spectra, concluded that 2-benzoylbenzamides (Ia–c) have structure A in the crystalline state and structure B in solution. We [2,3] and, independently of us, Flitsch [4], have shown that 2-acylbenzamides (including Ia–c) have only ring structure B in both the crystalline state and in solutions. Exceptions to this are cases in which the formation of the ring form is impossible because of the large volume of the substituent attached to the nitrogen atom [2,5] or the carbonyl group [6] and also because of the strong −I effect [7] of substituent R. There is an intense C = O bond at 1695–1720 cm^{-1} in the IR spectra of solutions of 2-R-substituted 3-hydroxy-3-phenylisoindolinones (IB). In the IR spectra of crystalline IB, this band is lowered to 1660–1680 cm^{-1} (and is sometimes split) as a result of the formation of C = O ··· H−O intermolecular hydrogen bonds and was erroneously taken [1] for the total $\nu_{C=O}$ band of the amide and $\nu_{C=O}$ of the diaryl ketone in 1A. However, the II amide band ($\delta_{N-H} + \nu_{C-N}$) is absent in the spectra of crystalline Ia,b, and a very broad band of associated O−H groups is observed at ~3300 cm^{-1}. The differences observed on comparison of these spectra with the spectra of N-(tert-alkyl)amides of 2-benzoylbenzoic acid [2] or 2-mesitoylbenzamides [7], which have structure A for steric reasons, confirm ring structure B for Ia–c in the crystalline state.



Ia–c

A B



II

A B

Ia R = H, b R = CH_3, c R = C_6H_5; II X = Cl, Br; R = H, Alk, Ar

A similar error occurs in the paper of Semonsky and co-workers [8]. Two C = O bands at 1700–1720 and 1685–1672 cm^{-1} are observed in the IR spectra of crystalline cis-β-(p-methoxybenzoyl)-β-haloacrylamides (II); Semonsky et al. assign the first band to the amide $\nu_{C=O}$ (which is improbably high for acrylamides) and the second band to aroyl $\nu_{C=O}$ (in structure A). The absence of an amide II band and the presence of a very broad ν_{O-H} band enable us to assert that in the crystalline state compounds II have structure B. This is in agreement with the data in [9–11] regarding the structure of other cis-β-acylacrylamides. The appearance of two C = O bands is explained by the presence of associated and unassociated carbonyl groups in the crystal lattice.

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