UDC 547.856 + 543.422.6

STRUCTURE AND ULTRAVIOLET ABSORPTION SPECTRA OF INDAZOLONES

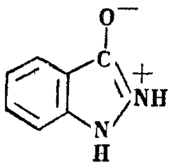
B. D. Chernokal'skii, A. T. Groisberg, N. F. Rakova, and R. R. Shagidullin

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 1, pp. 96-100, 1966

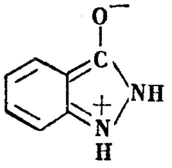
The UV spectra of indazolone and its derivatives are investigated, and hypotheses regarding their structure advanced. It is shown that the UV spectra of 1- and 2- acylindazolones have different characters, which can be utilized to identify those particular isomers.

It has been shown that the absorption spectra of indazolone and its 1-alkyl derivatives are very similar, and are independent of pH up to pH 7, though differing consideably from the light absorption curves of indazolone in alkaline solution, and of 2-phenylindazolone in methanol.

The structure of indazolone and its derivatives can be represented by a number of closely related structures. D. O'Sullivan [2] notes that the most important ones are I and II, as the IR spectrum of indazolone in the crystalline state possesses one wide absorption band in the 3100-2700 cm^{-1} region, connected with N–H valence vibrations.

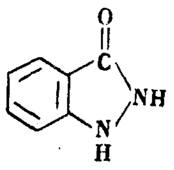


I

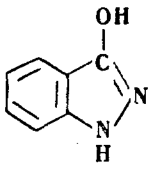


II

We consider that structures I and III more accurately represent the structure of indazolone in the solid state and in neutral solution. Thus indazolone, its 5-methyl and 5-nitro derivatives have an intense C=O absorption band at rather low frequencies (1630-1621 cm^{-1}), but lacks strong bands in the C–O valence vibrations region (1250-1000 cm^{-1}). A broad absorption band at 3100-2700 cm^{-1}, with a number of maxima, may also indicate N–H vibrations at non-equivalent nitrogen atoms. Further the facile isomerization [3, 4] of 2-acyl- into 1-acylindazolone derivatives is actually



III



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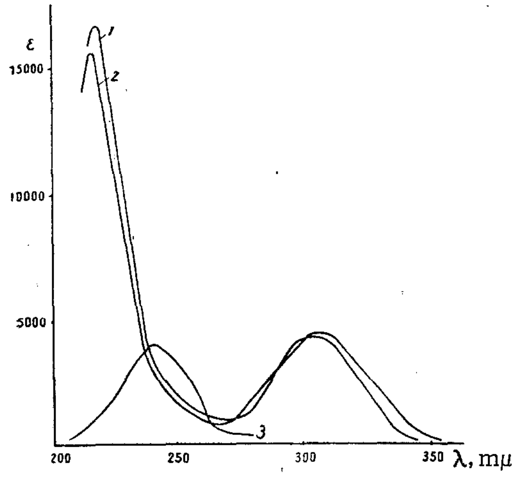


Fig. 1. UV spectra of indazolone in different solvents (concentration 10^{-4} M): 1) ethanol; 2) water; 3) dioxane.

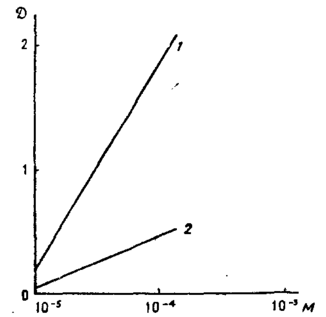


Fig. 2. Relationship between solution optical density and indazolone concentration in ethanol.

connected with localization of a positive charge on the second nitrogen atom. The greater contribution of form I, and the possibility of tautomerism (I ⇄ IV) in neutral polar solutions, are indicated by the similarity between the UV spectra [1] of indazolone and its 1-derivatives, their difference from the UV spectra of 2-derivatives, and also the identity of

Absorption Maxima of Indazolones with Substituents in the Benzene Ring
(in Ethanol Solution)

Expt. No.	Substituents and their positions	λ_{max}, mμ	lg ε	λ_{max}, mμ	lg ε
1	—	219	4.22	304	3.65
2	5-CH_3	218	4.22	315	3.60
3	5-Br	226	4.26	315	3.60
4	5-Cl	226	4.07	325	3.46
5	6-Cl	226	4.29	310	3.54
6	5.7-Cl_2	226	4.23	321	3.61
7	5-SO_3H	221	4.18	312	3.72
8	6-CH_3CONH	225	4.53	310	3.53
9	6-NO_2	262	4.18	—	—
10	4-NO_2	238	4.08	340	3.48
11	4-COOH	231	3.87	337	3.60

the shapes of the absorption curves for indazolone in acid and neutral solution. The UV spectra of indazolone in ethanol and water (Fig. 1) comprise two bands, a sharp short wave one (λ_{max} 219 and 217 mμ, lg ε 4.22 and 4.19), and a less intense long wave one (λ_{max} 304 and 307 mμ, lg ε 3.65). The near UV spectra in dioxane have only a second band (λmax 241 mμ, lg ε 3.60). The light absorption of solutions of indazolone in ethanol obeys the Lambert-Beer equation (Fig. 2).

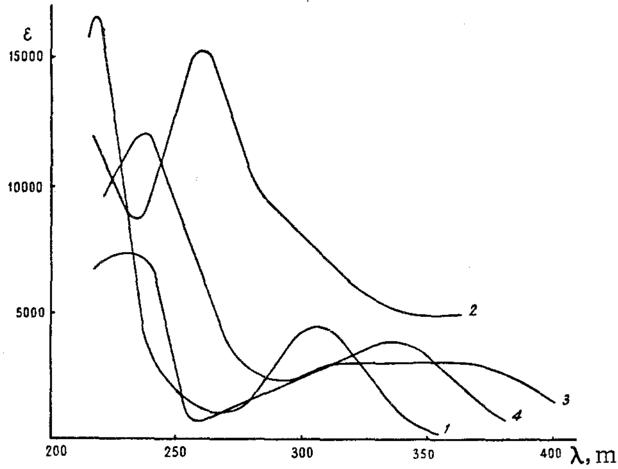
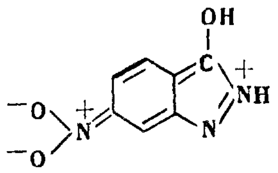


Fig. 3. UV spectra of ethanol solutions of indazolones with substituents in the benzene ring: 1) indazolone, 10^{-4} M; 2) 6-nitroindazolone, 0.8 × 10^{-4} M; 3) 4-nitroidazolone, 1.1 × 10^{-4} M.

Replacement of hydrogen in the benzene ring by halogen, methyl, or sulfonic acid groups has no significant effect on the UV spectra of indazolones (table, nos. 2-7). A two-fold increase in the intensity of the short wave band, obviously connected with lengthening of the conjugated chain, is characteristic of the spectrum of 6-acetoaminoindazolone. lone.

Probably the structure of the excited 6-nitroindazolone molecule is significantly displaced towards the side of the p-quinonoid structure V; its UV spectrum in ethanol is almost lacking in absorption in the 320 mμ region, and the increased polarity of the molecule gives rise to a bathochromic shift of the short wave band.



V

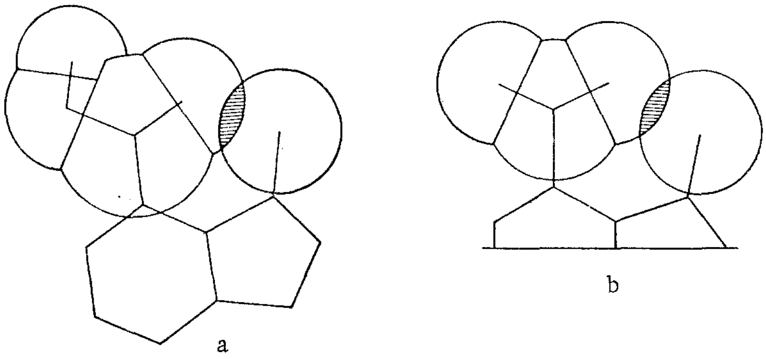


Fig. 4. Stuart-Brigleb molecule models: a) 4-carboxy-, and b) 4-nitroindazolone.

The structures of 4-nitro- and 4-carboxyindazolones can also be shifted towards an o-quinonoid structure. However, lowering of the intensity of absorption at 220 mμ indicates steric hindrance to conjugation of the nitro and carboxyl groups with the benzene ring. Stuart-Brigleb models of the molecules confirm this hypothesis (Fig. 4).

Their UV spectra are rendered more complex when the hydrogen at the nitrogen atoms is substituted by acyl (Fig. 5). 2-Acylindazolones have an absorption curve with two maxima in the short wave region, and 1-acyl derivatives in the long wave region. The clear differences between the UV spectra of the acylindazoles can be used, obviously, to ascertain the position of the acyl group. The absorption spectra of diacetylindazolone and 1-acetylindazolone closely resemble one another. In this connection it can appropriately be mentioned that a paper [4] considers diacetylindazolone to be a N, O derivative.

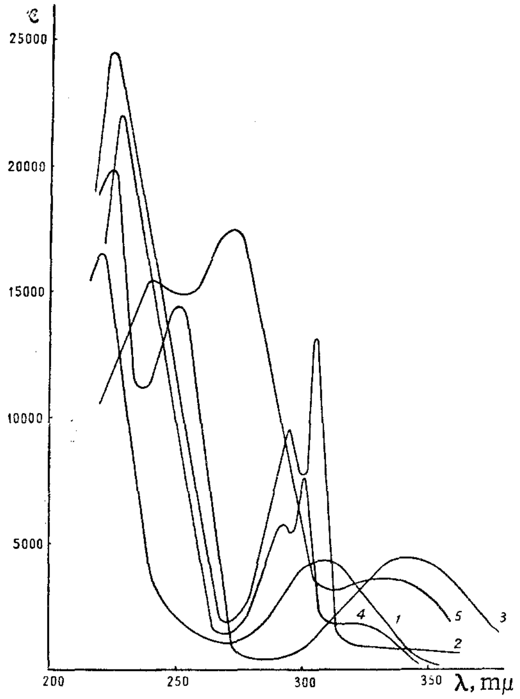


Fig. 5. Uv spectra of acylindazolones: 1) indazolone, 10^{-4} M; 2) 1-acetylindazolone, 10^{-4} M; 3) 2-acetylindazolone, 10^{-4} M; 4) diacetylindazolone 0.8×10^{-4} M; 5) 2-phenylcarbamylindazolone, 10^{-4} M.

Experimental

We have previously given information regarding synthesis of indazolones substituted in the benzene ring [5]. 2-Phenylcarbamyl- and acetylindazoles were synthesized by known methods [3, 4, 6]. The vibration spectra of the indazolones were studied with an IKS-14 spectrometer using LiF and NaCl prisms in the 3450-2200 and 1800-690 cm^{-1} regions. Specimens were tabletted with KBr. The absorption frequencies were (frequencies cm^{-1}, s = strong, a = = average, w = weak absorption):

Indazolone: 3062s, 2925s, 2840s, 2225w, 1627s, 1595a, 1497w, 1465a, 1412w, 1351a, 1333a, 1231w, 1161w, 1103w, 1089w, 1001w, 932w, 889a, 787a, 745s, 695a.

5-Methylindazolone: 3430w, 3125s, 2912s, 2773a, 2725a, 1630s, 1583a, 1503a, 1432w, 1350s, 1306a, 1258w, 1228w, 1107w, 1082a, 982a, 900w, 836a, 812a, 770a, 760a, 719w, 688a.

5-Nitroindazolone: 3385s, 3310s, 3200s, 2900s, 2705s, 1621s, 1565a, 1526a, 1468a, 1402w, 1345s, 1325s, 1280a, 1155a, 1100ω, 1048a, 915w, 856w, 815w, 796w, 742a.

The UV spectra were measured with a SF-4 spectrometer, in spectroscopic ethanol solution, purified dioxane, or water (twice distilled).

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4 March 1965

Kazan Branch of the All-Union Motion Picture Scientific Research Institute, Kirov

Kazan Institute of Chemical Technology