Brief Communications

Determination of the structure of 7-diethylamino-4-(1,2,3-triazol-1-yl)-2*H*-1-benzopyran-2-one derivatives using two-dimensional heteronuclear chemical-shift correlated NMR techniques

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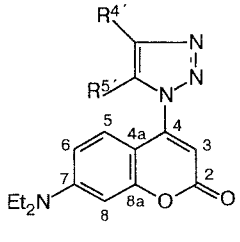
^{1}H and ^{13}C NMR spectra of 7-diethylamino-4-(1,2,3-triazol-1-yl)-2*H*-1-benzopyran-2-one derivatives have been studied. The location of the substituent in the 1,2,3-triazole ring was determined by the 2D COLOC method. It was established that the H(3) and H(5) protons in the coumarin moiety experience anisotropic influence of the phenyl subsituent at the C(5') atom in the triazole ring.

Key words: 7-diethylamino-4-(1,2,3-triazol-1-yl)-2*H*-1-benzopyran-2-ones; ^{1}H, ^{13}C NMR, two-dimensional NMR COLOC method.

NMR is extensively used for investigating the structure of 2*H*-1-benzopyran-2-one (coumarin) derivatives[1—8] and substituted 1,2,3-triazoles.[9,10] In the present work we studied the ^{1}H and ^{13}C NMR spectra of novel 7-diethylamino-4-(1,2,3-triazol-1-yl)-2*H*-1-benzopyran-2-one derivatives (**1—5**) prepared by the reaction of 4-azido-7-diethylaminocoumarins with substituted alkynes.* Therefore, the position of the substituent in the 1,2,3-triazole ring needed to be determined.

1: $R^{4'}$ = H, $R^{5'}$ = Ph
2: $R^{4'}$ = Ph, $R^{5'}$ = H
3: $R^{4'}$ = Ph, $R^{5'}$ = Ph
4: $R^{4'}$ = CH_2Cl, $R^{5'}$ = H
5: $R^{4'}$ = CH_2OH, $R^{5'}$ = H



Chemical shifts of the coumarin moiety (Table 1) coincide with the literature data.[8] The signal of the proton in the triazole ring can be easily distinguished, since it is located furthest downfield.

In a number of works, the assignment of the ^{13}C signals of coumarins has been confirmed by the analysis of the ^{13}C—^{1}H spin coupling using «tickling» experi-

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* The preparation of compounds **1—5** will be described in detail in a separate communication.

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Table 1. Parameters of ^{1}H NMR spectra of compounds **1—5**

Com-	δ								
pound*	H(3)	H(5)	H(6)	H(8)	H(4′)	H(5′)	CH_3	CH_2	Other protons
1	5.87	7.09	6.56	6.58	7.98	—	1.24	3.45	Ph: 7.3—7.4
2	6.22	7.77	6.64	6.60	—	8.31	1.27	3.48	Ph: 7.4—8.0
3	5.80	7.25	6.62	6.59	—	—	1.27	3.49	Ph: 7.3—8.0
4	6.12	7.59	6.61	6.58	—	8.06	1.23	3.45	CH_2: 4.83
5	6.13	7.61	6.59	6.56	—	8.04	1.23	3.45	CH_2: 4.96

* Spin coupling constants $^3J_{5,6}$ = 9.04, $^4J_{6,8}$ = 2.4 Hz are observed for all of the compounds.

ments and «off-resonance» techniques.[2—5,7] The ^{13}C NMR signals (Table 2) were assigned on the basis of the analysis of proton-coupled spectra. For this purpose we used methods of two-dimensional spectroscopy, XHCORR[11] and COLOC[12] for the short-range and long-range ^{13}C—^{1}H spin coupling constants, respectively.

The ^{13}C signals for the phenyl groups and C(5) with close chemical shifts in the spectra of compounds **1—3** were assigned using the XHCORR heteronuclear corre-

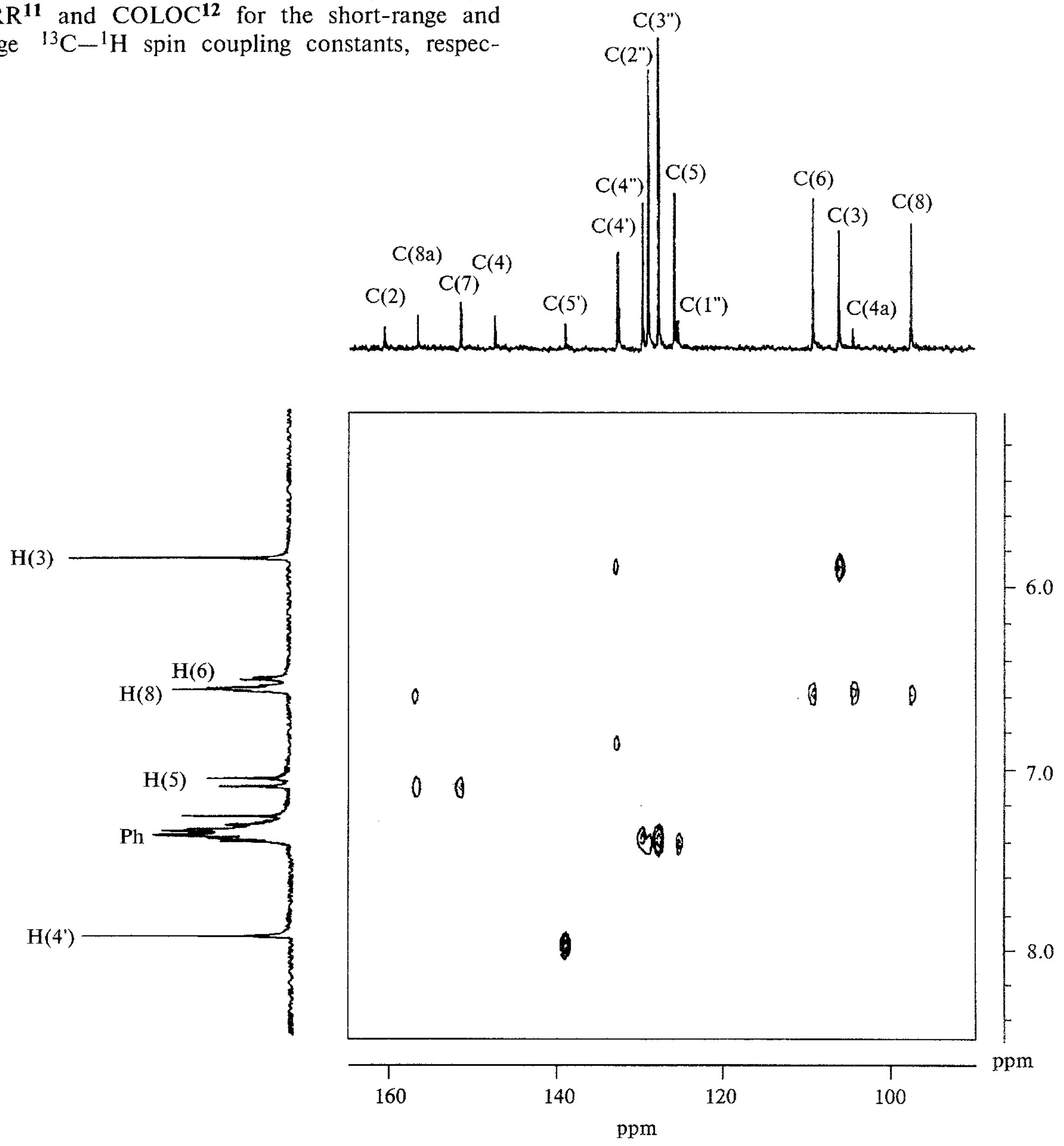

Fig. 1. The processed 2D COLOC spectrum of compound **1** optimized for 14 Hz.

Table 2. ^{13}C NMR chemical shifts for compounds **1—5**

Compound	δ													
	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(4a)	C(8a)	C(4′)	C(5′)	CH_3	CH_2	Other
1*	160.67	106.21	147.56	125.98	109.33	151.87	97.55	104.53	156.82	132.75	139.07	12.27	44.50	—
2*	161.13	101.58	147.04	126.60	109.34	151.57	97.73	102.72	157.07	148.06	120.20	12.32	44.61	—
3*	160.88	106.52	147.21	125.15	109.38	151.68	97.63	105.09	156.76	144.55	134.80	12.39	44.88	—
4	160.85	101.95	146.80	126.24	109.31	151.58	97.71	102.51	156.99	145.22	123.33	12.21	44.77	CH_2:35.45
5	161.31	101.85	147.21	126.53	109.45	151.70	97.81	102.74	157.13	148.33	122.61	12.36	44.89	CH_2:56.44

* Chemical shifts of the phenyl ring carbon atoms are not presented.

lation method (the parameters were selected for $^1J_{CH}$ = 160 Hz). The location of substituent R in the triazole ring was determined from the chemical shifts and ^{13}C—^1H spin coupling constants based on the literature data (see Refs. 9, 10). To assign the ^{13}C signals for the quaternary carbon atoms of the triazole ring and the coumarin moiety we used the 2D COLOC method, which allows one to observe the long-range heteronuclear spin coupling constants.[13]

Figure 1 shows the processed 2D COLOC spectrum of compound **1** optimized for 14.0 Hz. The signals of the quaternary carbon atom of the triazole ring can be easily assigned, since the spectrum exhibits a cross peak, which correlates this carbon atom with the low-field proton of the triazole. The magnitude of the chemical shift of this carbon atom (see Table 2) allows its assignment to position C(5′) (see Ref. 10).

The validity of the structures ascribed to compounds **1—3** is also supported by the fact that the H(3) and H(5) signals in the spectra of compounds **1** and **3** are shifted 0.25—0.42 ppm upfield with respect to those of compound **2**, as a result of the magnetic anisotropy[13,14] of the phenyl substituent in the triazole ring. It should be noted that in compounds **1** and **3** both these protons experience the shielding effect caused by the phenyl ring. In compound **2** this effect is considerably weaker due to the remoteness from the H(3) and H(5) protons. This is probably due to hindered rotation of the 1,2,3-triazole ring about the C(4)—N(1) single bond.

Thus, we assigned all of the ^1H and ^{13}C NMR signals for compounds **1—5**. The determination of the position of the substituent in the triazole ring allowed us to identify the products of the reaction of 4-azido-7-diethylaminocoumarins with substituted alkynes.

Experimental

^1H and ^{13}C NMR spectra of compounds **1—5** (100—200 mg mL^{-1}) were recorded on a Bruker AC(2)00 NMR spectrometer in $CDCl_3$ (^1H 200.13, ^{13}C 50.33 MHz) with TMS as the internal standard. To record 2D spectra, standard XHCORR and COLOC software (Bruker) were used.

References

1. H. Gunter, J. Prestien, and P. Joseph-Nathan, *Org. Magn. Reson.*, 1975,**7**, 339.
2. S. A. Sojka, *J. Org. Chem.*, 1975, **40**, 1175.
3. N. J. Cussans and T. N. Huckerby, *Tetrahedron Lett.*, 1975, 3445; Idem., *Tetrahedron*, 1975, **31**, 2591, 2719.
4. C.-J. Chang, H. G. Floss, and W. Steck, *J. Org. Chem.*, 1977, **42**, 1337.
5. K. K. Chan, D. D. Giannini, A. H. Cain, J. D. Roberts, W. Porter, and W. F. Trager, *Tetrahedron*, 1977, **33**, 899.
6. V. S. Parmar, S. Singh, and P. M. Boll, *Magn. Reson. Chem.*, 1988, **26**, 430.
7. A. Osborne, *Magn. Reson. Chem.*, 1989, **27**, 348.
8. M. A. Kirpichenok, S. K. Gorozhankin, and I. I. Grandberg, *Khim. Geterotsikl. Soedin.*, 1988, 751 [*Chem. Heterocycl. Compd.*, 1988 (Engl. Transl.)].
9. A. Bojilova, N. A. Rodios, C. A. Tsoleridis, and N. E. Alexandrou, *J. Heterocyclic Chem.*, 1990, **27**, 735.
10. M. Begtrup, J. Elguero, R. Faure, P. Camps, C. Estopa, D. Ilavsky, A. Fruchier, C. Marzin, and J. de Mendoza, *Magn. Reson. Chem.*, 1988, **26**, 134.
11. A. Bax and G. Morris, *J. Magn. Reson.*, 1981, **42**, 501.
12. H. Kessler, C. Griesinger, J. Zarbock, and H. R. Loosli, *J. Magn. Reson.*, 1984, **57**, 331.
13. J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.*, 1966, **88**, 4811.
14. C. W. Heigh and R. B. Mallion, *Org. Magn. Reson.*, 1972, **4**, 203.

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