

VICINAL ^{13}C - ^{13}C COUPLING VIA N=N, N=NO AND C=N PATHS

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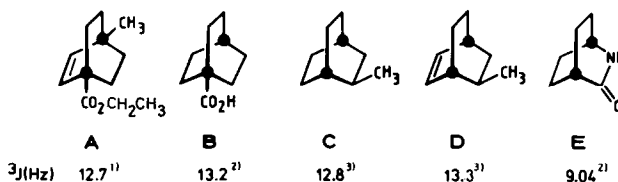
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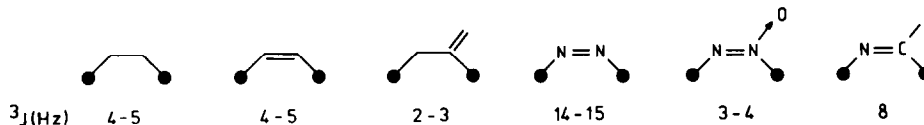
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SUMMARY: From the vicinal ^{13}C - ^{13}C coupling constants determined for a series of bi(poly)cyclic azo-, azoxy- and imino-compounds an independent increment for the N=N-, N=NO- and N=C units of ca. 15, 3-4 and ca. 8 Hz resp. was deduced.

^{13}C - ^{13}C coupling constants are increasingly used for structural analyses. A more profound knowledge about their dependence on structural features is therefore highly desirable. With respect to vicinal ^{13}C - ^{13}C coupling, the concept of additivity of coupling contributions through multiple pathways has been invoked to explain the relatively large coupling constants between the bridgehead carbon atoms in bicyclo[2.2.2]octanes(enes) ¹⁻³. Contributions for individual coupling paths in the representative structures A-D amount to 4-5 Hz, in agreement with calculations ⁴⁻⁶. In

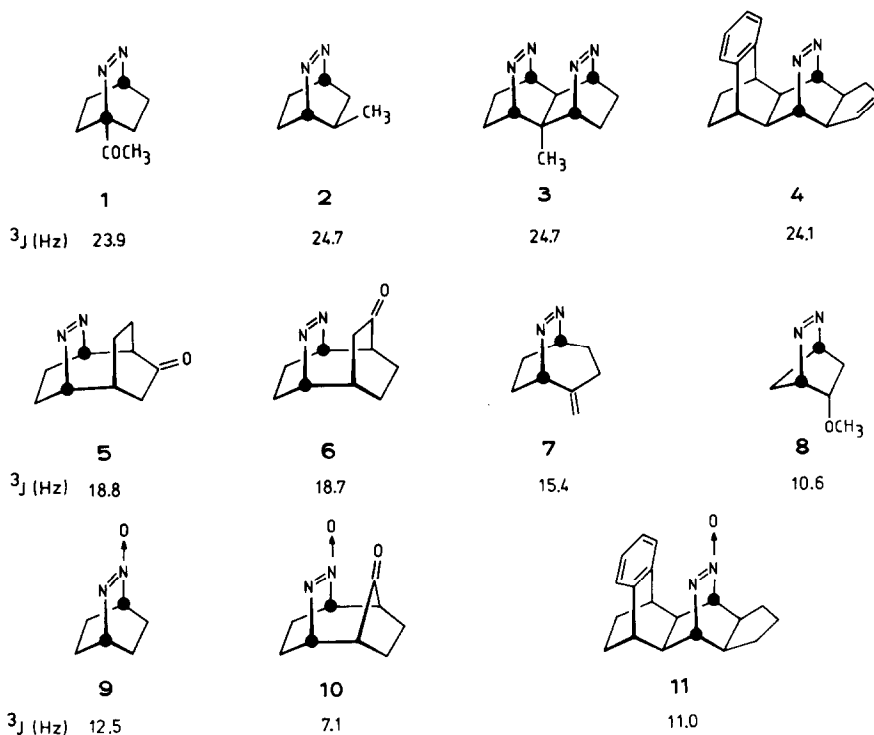


one single case (E) so far, the influence of heterosubstitution in the bridges upon the magnitude of this vicinal ^{13}C - ^{13}C coupling was studied ²⁾. The amide bridge in E (10.7 Hz calc. ²⁾) is obviously a poor transmitter. In this communication we report on the increments provided by azo-, azoxy- and



imino-paths in similar sterically fixed skeletons.

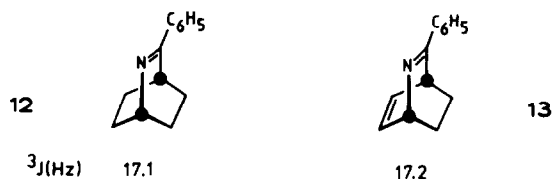
In the course of our studies centered on the quality of the azo-/azoxy-chromophoric units as π 2-components in photochemical/thermal cycloaddition reactions ^{7,8}, a series of novel bi(poly)cyclic azo(azoxy)-compounds (i.e., the unsymmetrical 3, 4, 6, 7, 11) became available. During their structural elucidation by NMR-spectroscopy, some surprisingly large ³J-coupling constants between the bridgehead carbon atoms for the unsymmetrical members were observed. These data, together with the ones for some specifically prepared analogues (1, 2, 5, 8, 9, 10) are listed in Scheme 1. The values determined for the diazabicyclo[2.2.2]octenes 1-4 with three vicinal paths,



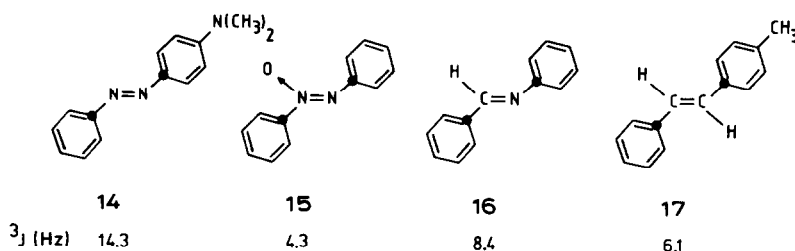
when compared with their carbocyclic analogues A-D, allowed the conclusion, that the coupling across the N=N double bond is unusually effective, adding ca. 15 Hz to the total value. An increment of similar magnitude can be deduced from the ³J-values measured for the azo-compounds 5-7, which feature two vicinal coupling paths (it is assumed, that the two additional paths over five C-C bonds in 5/6 make a negligible contribution and the one over four C-C bonds in 7 a weakly negative contribution). The ³J-value for the bicyclo[2.2.1]-compound 8 is smaller than expected on the basis of the known negative contribution of the geminal path of 2-3 Hz ^{2,3,6}.

Due to preparative reasons only the three mono-azoxy-derivatives 9-11 (Scheme 1) were available. From these three cases which have three and two vicinal paths, it becomes clear that oxidation of the azo-bridge strongly reduces the azo-increment.

The extension of this study to bi(poly)cyclic imines, which incorporate at least one C=N path, was problematic because of the difficulties in preparing and handling such compounds. As judged by the limited data on 12-13, the contribution of the C=N-unit is approximately half of the one of the N=N-unit.



Finally, in the model systems 14-17, the azo-, azoxy-, imine- and ene-units are trans-fixed to two sp^2 -carbon atoms. Again, this single path vicinal coupling depends intimately on the nature of the intervening



fragment, manifesting a trend rather similar to the one in the above polycyclic skeletons.

EXPERIMENTAL:

Compounds 1, 3, 4, 6, 7, 10, 11 were prepared in connection with the above mentioned photochemical investigations ^{7,8}. The syn/anti-differentiation between 6 and 7 rests on the X-ray analysis of the syn-azo/ene ($d_{C=C/N=N} = 2.70 \text{ \AA}$) derived from 6; the syn-orientation of the azo/benzo-units in 4 (m.p. 279°C, $\lambda_{max}(\epsilon) = 391 \text{ nm (150), 377 (90), 273 (sh, 260), 264 (sh, 405); CH}_3\text{CN)/11 (m.p. 290°C, } \lambda_{max}(\epsilon) = 274 \text{ nm (sh, 790), 247 (sh, 2300)}$) is proven by an X-ray analysis of dihydro-4 (\equiv deoxy-11) (m.p. 215°C, $d_{C=C/N=N} = 2.97 \text{ \AA}$). The experimental/analytical details will be given in the full papers. Compounds 5 ⁹, 8 ¹⁰, and 9 ¹¹ have been prepared according to literature procedures. 2 (oil, $\lambda_{max}(\epsilon) = 381 \text{ nm (10), 371 (sh, 60), 344 (20); CH}_3\text{CN}$) was synthesized from 2-methyl-cyclohexadiene ¹² and 4-methyl-1,2,4-triazolinedione, 12 (m.p. 64°C, $\lambda_{max}(\epsilon) = 241 \text{ nm (13600); CH}_3\text{CN)/13 (m.p. 38°C, } \lambda_{max}(\epsilon) = 243 \text{ nm (10600); CH}_3\text{CN}$) starting from the known 3-phenyl-2-azabicyclo[2.2.2]oct-5-ene-2-ethylcarboxylate ¹³ ($(\text{CH}_3)_3\text{SiI, CH}_3\text{OH, N-chlorosuccinimide; KOH; H}_2/\text{Pd(C)}$).

All ^{13}C NMR spectra were recorded in natural abundance on a Bruker WM 400 spectrometer at 100.6 MHz, solvent CDCl_3 , 5 mm tubes, 25°C , concentrations ca. 200 mg/ml, digital resolution better than 0.2 Hz. The ^{13}C - ^{13}C coupling constants (± 0.2 Hz) were obtained either from the ^{13}C satellites of the ^1H broad band decoupled spectra or from INADEQUATE measurements ⁽⁴⁾.

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