Mais il existe d'autre part la possibilité pour cet ion de se réarranger en une forme plus stable. Nous avons vu qu'on peut se représenter cette nouvelle structure comme celle d'un cyclobutane protoné. La stabilité de cette forme n'est d'ailleurs pas absolue et une fragmentation peut intervenir après le réarrangement⁶). Dans le premier cas, la constante de vitesse dépend essentiellement de l'énergie interne de l'ion butyle, alors que dans le cas du réarrangement, c'est avant tout l'entropie de la réaction qui détermine la vitesse avec laquelle l'ion se transforme. Par conséquent, l'augmentation de la complexité du réarrangement nécessaire à la cyclisation favorise la décomposition directe. Ceci explique la différence observée entre l'ion butyle primaire et le tertiaire.

Notons enfin qu'il serait intéressant de connaître la chaleur de formation de l'ion butyle réarrangé, ainsi que les énergies d'activation associées au réarrangement des différents isomères. De cette manière nous saurions dans quelle mesure cette nouvelle structure est plus stable que les formes connues jusqu'à présent et si les ions butyle parvenant intacts sur le collecteur ont pour la plupart conservé leur structure originale ou s'ils se sont réarrangés.

Nous tenons à remercier MM. *F. Etzweiler*, *J. P. Müller* et *B. Wirz* de leurs travaux de synthèses, et le *Fonds National* de l'aide accordée pour ce travail.

BIBLIOGRAPHIE

[1] *R. Liardon & T. Gäumann*, Helv. *52*, 1042 (1969).
[2] *R. Liardon & T. Gäumann*, Helv. *52*, 528 (1969).
[3] *M. S. B. Munson*, J. Amer. chem. Soc. *89*, 1773 (1967).
[4] *B. Davis, D. H. Williams & A. N. H. Yeo*, J. chem. Soc. *B* 1970, 81.
[5] *I. Hertel & C. Ottinger*, Z. Naturforsch. *22a*, 1141 (1967).
[6] *H. D. Beckey, H. Hey, K. Levsen & G. Tenschert*, Internat. J. Mass Spectr. *2*, 101 (1969).
[7] *S. G. Lias, R. E. Rebbert & P. Ausloos*, J. Amer. chem. Soc. *92*, 6930 (1970).
[8] *C. P. Johnson & A. Langer*, J. physic. Chemistry *61*, 891, 1010 (1957).
[9] *H. M. Grubb & S. Meyerson* dans «Mass Spectrometry of Organic Ions», *F. W. McLafferty*, Ed., Academic Press, New York 1963.

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⁶) Une estimation du taux de fragmentation montre qu'à 70 eV, 60 à 65% des ions butyle formés dans la source se décomposent avant de parvenir sur le collecteur. L'importance de cette fraction ne dépend que très peu de la structure originale des ions $C_4H_9^+$.

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211. Theoretical Study of the Structure and the Physico Chemical Properties of 1,2-Benzyne

by **E. Haselbach**

Physikalisch-Chemisches Institut der Universität Basel

(6. VII. 71)

Summary. The structure of 1,2-benzyne (I) has been optimized with respect to its total molecular energy using the MINDO/2 SCF-procedure. The results indicate a bond length of ~1.26 Å for the strained triple bond. The overall geometry suggests that I possesses considerable resonance energy. The calculated heat of formation ($\Delta Hf(\mathrm{I}) = 107$ kcal/mole) is in good agreement with an estimate from mass spectrometric studies ($\Delta Hf^{\mathrm{exp}}(\mathrm{I}) = 118 \pm 5$ kcal/mole). From model calculations for bent acetylene the strain energy of I is estimated to be about 60 kcal/mole. Some chemical reactions of I are discussed in the light of the results.

Introduction. – 1,2-benzyne (I) is of interest to organic chemists as an intermediate in numerous chemical reactions [1].

Recently an *ab-initio* study of 1,2-benzyne (I) has been reported by *Millie, Praud & Serre* [2]. While their results concerning the electronic structure of I are valuable, their calculated heat of formation ΔHf (I) = 72.6 kcal/mole is in serious disagreement with an estimate obtained from mass spectrometric studies [3] (ΔHf^{exp} (I) = 118 ± 5 kcal/mole, [3], tab. 1). The calculated value is obtained by adding ΔHf (benzene) = 19.8 kcal/mole to the energy necessary to abstract two hydrogen atoms from benzene as calculated in [2] (157 kcal/mole) and subtracting from this sum the bond-energy of H_2 (104.2 kcal/mole [6]). However, the calculations [2] are based on the questionable assumption that the interatomic distances in 1,2-benzyne are the same as in benzene (D_{6h}-symmetry, C=C : 1.397 Å, C–H : 1.084 Å). *Coulson* [8] found for the strained "triple bond" in I a bond order of 2.855, which would indicate a considerable shortening from the normal aromatic bond length. According to a theoretical study of *Yonezawa, Konishi & Kato* [9] this shortening should be at least 0.1 Å. Extended *Hückel* calculations performed by *Hoffmann, Imamura & Hehre* [10] also indicate a rather short C(1)-C(2) bond.

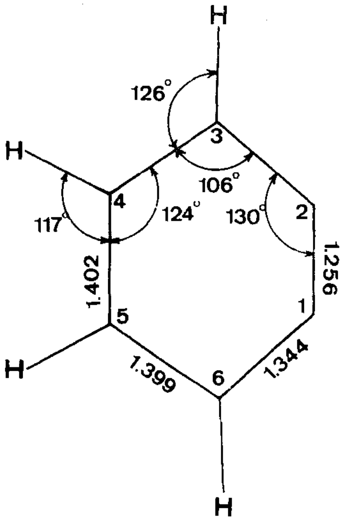
Table 1. *MINDO/2 and* ab-initio *results* [2] *for the heat of formation* (ΔHf) *and first ionization potential* (IP) *for benzene and 1,2-benzyne in comparison with experimental data*

Compound	Theoretical Results				Experimental Results	
	this work		ref. [2]			
	ΔHf (kcal/mole)	IP a) (eV)	ΔHf (kcal/mole)	IP a) (eV)	ΔHf (kcal/mole)	IP (eV)
Benzene (D_{6h})	20.1	9.63 e_{1g} (π)		11.62 b) e_{1g} (π)	19.8 [6]	9.20 [3] 9.50 [7]
Ia 1,2-benzyne (benzene-like structure ass.)	128.3	8.49 a_1 (σ)	72.6	11.22 a_1 (σ)	118 ± 5 [3]	9.45 [3] 9.75 [7]
I 1,2-benzyne (C_{2v}, optimised)	107.1	8.68 a_1 (σ)				

a) Assuming *Koopmans'* theorem [4].
b) From ref. [5], cited in [2].

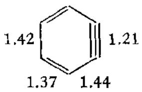
We report now some calculations on I, using the semi-empirical MINDO/2 SCF-procedure [11], which has proved to yield heats of formation, geometries and force constants with reasonable accuracy for a great number of compounds containing C-, H-, N- and O-nuclei. In addition, we have also calculated the energy associated with a bending deformation of acetylene, since this might provide an estimate of the strain present in I.

Results and discussion. – *A. Molecular geometry and heat of formation of* 1,2-*benzyne.* Energy minimization leads to the structural data depicted in the figure (geometrical constraints used in the minimization process: C_{2v}-symmetry; C–H = 1.084 Å).

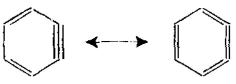


Structural data of 1,2-benzyne

The calculated structure is considerably different from that of benzene, the strained "triple bond" being only 0.05 Å longer than in acetylene (1.205 Å [12]). This is in line with chemical intuition and also with theoretical considerations [8–10]. The C(2)-C(3) and C(1)-C(6) bonds are also shortened by about 0.05 Å compared with benzene. Compared with an (unstrained) C_{sp^2}-C_{sp} essential single bond, such as in methyl-vinyl-acetylene (1.43 Å) [12], the shortening is 0.085 Å. This indicates that considerable π-electron delocalization prevails in I, a conclusion also supported by the lengths obtained for the C(5)-C(6) and C(4)-C(5) bonds, which are both nearly the same as in benzene. These results differ from *Coulson*'s [8] bond-length estimates,



which would imply that I is a "cyclodiene-yne". In contrast, our results support *Hoffmann*'s suggestion [10] that a sizeable resonance contribution comes from the cumulene structure Ib:



I Ib

As expected, the bond angles in I deviate from 120°. In particular, the C(1)-C(2)-C(3) angle increases by about 10°. Calculations in which the optimal bond lengths are kept constant while the angles are varied indicate that further increase in the C(1)-C(2)-

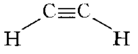
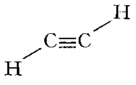
C(3) angle leads to a further decrease in electronic energy which, however, is overcompensated by increase in transannular nuclear repulsion.

The heat of formation for I is found to be ΔHf(I) = 107 kcal/mole (tab. 1), in good agreement with the value obtained by *Gruetzmacher & Lohmann* [3] (ΔHf^{exp}(I) = 118 ± 5 kcal/mole) from electron impact studies, especially if one allows for the slight underestimation of strain energies by the MINDO/2-method [11]. We have also calculated ΔHf, assuming the benzene-like structure suggested in [2], with the C-C bond lengths taken as 1.383 Å, the value obtained by minimizing the energy of benzene with the MINDO/2-method. We obtained ΔHf(Ia) = 128 kcal/mole or about 21 kcal/mole higher than that for the optimized structure of C_6H_4(I) discussed above (tab. 1). The energy increase is roughly that needed to stretch the C≡C bond in acetylene by 0.13 Å (force constant: $k = 14.9 \cdot 10^5$ dyn/cm [1]).

The calculated difference ΔHf(Ia)-ΔHf(I) = 21 kcal/mole can be subtracted from the value obtained in [2] in order to compensate for the incorrect geometrical assumptions made therein. The corrected value of ΔHf = 51.6 kcal/mole is now in even worse agreement with ΔHf^{exp}(I). This suggests that the second-order perturbation calculation performed in [2] is inadequate to account for the correlation energy in C_6H_4.

B. Bending of acetylene; the strain energy in 1,2-benzyne (I). We have also investigated the energy associated with bending one or both hydrogens of acetylene (II) out of colinearity with the triple bond. Tab. 2 shows the four nuclear arrangements considered, their calculated heats of formation (ΔHf), the interelectron and internuclear repulsion energy (E_{ee} and E_{nn}) and the nuclear-electron attraction energy (E_{ne}). The electronic energy E is the sum of E_{ne} and E_{ee}. Bond lengths assumed in calculations IIa, b, c are those obtained by energy minimization for linear acetylene (II) (see tab. 2). Bending one hydrogen atom by 60° (IIa) leads to an increase in molecular energy by 20.5 kcal/mole, in agreement with the estimate of 20 kcal/mole obtained with the bending force constant $k = 0.24 \cdot 10^{-11}$ dyn cm/rad^2 [1], assuming a harmonic potential. It is interesting to note that IIa possesses a more favorable electronic (E) than II. A further destabilization occurs when the second hydrogen atom is bent out, leading to the *cis*- or *trans*-structures IIb or IIc. Again the two

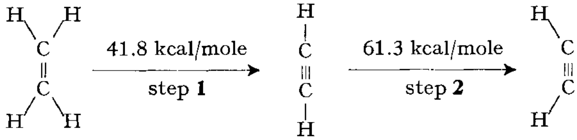
Table 2. *Model calculations on the bending of acetylene (see text)*

Compound		ΔHf (kcal/mole)	$-E$ (eV)	$-E_{ne}$ (eV)	E_{ee} (eV)	E_{nn} (eV)
II	H–C≡C–H	57.6 (54.3 exp. [6])	548.88	928.42	379.54	263.04
IIa[a]		78.1	551.15	933.38	382.24	266.20
IIb[a]		118.9	553.32	940.49	387.17	270.14
IIc[a]		86.6	553.49	937.17	383.68	268.91

[a] H–C–C angle = 120°, assumed.

processes IIa → IIb, IIa → IIc are accompanied by a decrease in E by almost the same amount, so that the relative stability of IIb and IIc depends virtually on the internuclear repulsion energy (E_{nn}), which is obviously greater in IIb. *Kollmar* [13] has found a similar behaviour for ethylene, where *trans*-bending of the CH_2-groups needs less energy than *cis*-bending. In view of the dominant *anti*-character of addition and elimination reactions involving double and triple bonds, as well as eliminations forming them, it seems that any reasoning about the reaction mechanisms should include internuclear repulsion arguments. This should be emphasized since there is a tendency to discuss chemical reactivity solely in terms of orbital-energies and -symmetries¹).

These calculations provide an estimate of the energy needed for abstracting hydrogen from ethylene, leading to the *cis* bent acetylene IIb.



II IIb

Step **1** in the diagramm is endothermic by the difference between $\Delta Hf(\mathrm{II}) = 54.3$ kcal/mole [6] and $\Delta Hf(C_2H_4) = 12.5$ kcal/mole [6]. For step **2** we use the calculated energy difference (tab. 2) to obtain an overall endothermicity of 103 kcal/mole. The experimental energy of hydrogen abstraction from benzene, leading to 1,2-benzyne, is 98 ± 5 kcal/mole. The good agreement between these energies suggests that the strain energy of 1,2-benzyne is about 60 kcal/mole, *i.e.* similar to the energy change associated with step **2**.

A final comment concerns the energy of the perturbed π-MO in the *cis*- and the *trans*-structures IIb and IIc, relative to II. Naive arguments imply that for both distortions this π-level should be stabilized since the hydrogen atoms move into a favorable overlap situation. However, the calculations show that the π-level in IIb lies above that of II. This feature is easily explained with reference to the symmetries of the MO's in IIb (C_{2v}-symmetry) and IIc (C_{2h}-symmetry). Even by setting up qualitative MO's for II one finds that for *cis*-bending, *i.e.* II → IIb, the relevant π-MO aquires the same symmetry (A_1) as the lower-lying C—C σ-bond MO. This leads to increasing repulsion [15] between these two levels with decreasing HCC-angle, resulting in destabilization of the higher-lying component. In case of *trans*-bending, these arguments do not apply, and the π-MO behaves as expected from pure overlap and hybridization considerations. (Note also the EHT-studies in [10] on the relative ordering of the MO's in such systems.)

C. Electronic structure and ionization potentials of 1,2-*benzyne* (*I*). The electronic structure of I obtained from the MINDO/2 calculations parallels that obtained in [2]. The highest occupied MO is of σ-type (symmetry A_1 in C_{2v}), localized mainly on C(1) and C(2). As pointed out in [2], this MO is in a sense a "π-orbital" since its major contribution stems from the in-plane p-AO's with parallel axes, centered at C(1) and C(2). Two nearly degenerate benzenoid π-orbitals follow, about 1 eV lower in energy. This conflicts with an earlier suggestion by *Berry, Spokes & Stiles* [16] that the highest occupied MO in I is benzenoid. However, there is a discrepancy between the theoretical results obtained here and in [2] with regard to the experimental ionization

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¹) *Sustmann et al.* [14] have recently found that the greater thermodynamic stability of i-$C_3H_7^+$ *vs.* n-$C_3H_7^+$ is due to a lower nuclear repulsion energy in the former.

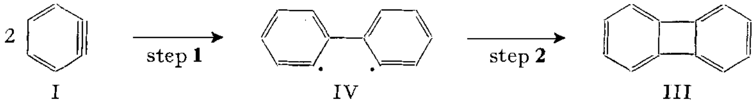
potentials (Tab. 1). The MINDO/2-calculations suggest that the first ionization potential (IP) of I should be lower by about 1 eV than that of benzene. The *ab-initio* results [2] lead to a difference of 0.4 eV in the same direction. This difference would probably decrease but not reverse sign if the proper geometry for I is used (*cf.* Tab. 1). In contrast, the experimental IP of I is higher than that of benzene by 0.25 eV [3, 7]. The uncertainties in extrapolating ion-currents in the mass-spectrometric estimation of ionization potentials are unlikely to account for the discrepancy in this particular case. It is well known from various calculations, *e.g.* on benzene [17], that an inadequate set of basis functions leads to too high-lying σ-MO's relative to the π-MO's. This might be the source of the trouble in the present case, since both calculations predict the highest σ-MO of I to be above the highest π-MO of benzene.

Conclusions. – The calculations reported in this paper support the experimental value of the heat of formation of 1,2-benzyne. Furthermore, the structural parameters obtained by energy-minimization suggest that I might possess considerable resonance energy and might therefore be called an "aromatic" system [*cf.* [18]). This resonance energy is, of course, overcompensated by a strain energy of the order of 60 kcal/mole. However, even this large destabilizing factor does not suffice to open uni-molecular isomerization or decomposition channels, as also indicated by experiment [1]. By estimating the enthalpies of reaction for all reasonable ring-opening and fragmentation reactions, using experimentally determined or estimated heats of formation for the products, one finds indeed endothermicity in all cases.

The lowest endothermicity obtained is for the isomerization of I to the open-chain C_6H_4-species, 1-hexene-3,5-diyne and 3-hexene-1,5-diyne, resp. ΔHf of these compounds can be estimated by adding ΔHf (1,3,5-hexatriene) = 40 kcal/mole [6] to the difference between ΔHf (diacetylene) = 113 kcal/mole [6] and ΔHf (1,3-butadiene) = 26.3 kcal/mole [6], leading to $\Delta Hf(C_6H_4$, open-chain) = 126.7 kcal/mole. This value, compared with $\Delta Hf^{\mathrm{exp}}(I)$, yields a heat of reaction for the process considered of about 10 kcal/mole.

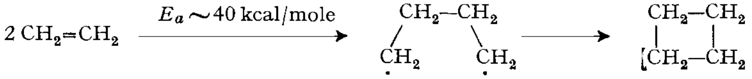
The apparent thermodynamic stability of I with respect to the monomolecular decomposition products considered above suggests that it could possibly be isolated under suitable conditions, perhaps in a matrix. Chemically, I exhibits high kinetic instability with respect to bimolecular reactions such as additions of nucleophiles, electrophiles or dienes. These features can be ascribed to the fact that I possesses a rather high-lying σ-MO with an electrical center of gravity situated in the molecular plane and rather distant from the nuclear skeleton. Frontier-electron [19] and stereochemical arguments would suggest that this MO will interact readily with those of suitable substrates.

In the absence of other attacking reagents, I dimerizes to biphenylene (III). This process can be estimated to be exothermic by about 120 kcal/mole, using ΔHf(III) = 115.3 kcal/mole [6]. From orbital symmetry arguments [20] or from *Evans'* principle [21] a concerted approach of two benzyne units is forbidden. The dimerization may thus involve the biradical intermediate IV as also indicated by the activation entropy for this process [22].



Dimerizations of that type do not usually occur from the ground states of the reactants (perhaps because of the unfavourable activation entropy) even in cases for which the activation energy – assumed to be approximately equal to the energy difference between biradical intermediate and reactants – lies within reasonable limits, being *e.g.* less than that for the converse (observable) ring-opening reaction.

As an example, we have tried to estimate in two ways the activation energy (E_a) for the hypothetical dimerization of ethylene to cyclobutane.



The experimental activation energy for the reverse process, *i.e.* the ring-opening of cyclobutane is 62.5 kcal/mole [23]. From ΔHf (ethylene) $= 12.5$ kcal/mole [6] and ΔHf (cyclobutane) $=$ 6.4 kcal/mole [6] we obtain $E_a \sim 44$ kcal/mole. On the other hand adding twice the difference between ΔHf (ethyl) $= 25.7$ kcal/mole [24] and ΔHf (ethane) $= -20.24$ kcal/mole [6] to ΔHf (butane) $= -30.2$ kcal/mole [6] and subtracting from this twice ΔHf (ethylene) yields $E_a \sim 36.7$ kcal/mole.

However, an estimate of ΔHf(IV) by adding twice the difference between ΔHf (phenyl) $= 80$ kcal/mole [25] and ΔHf (benzene) to ΔHf (biphenyl) $= 40.5$ kcal/mole [6] leads to a value of 160 kcal/mole, which, compared with twice ΔHf(I), yields an energy liberation of about 76 kcal/mole for step **1**! It is therefore not surprising that even a non-concerted dimerization of I will occur rapidly.

This work is part of project No. SR 2.120.69 of the *Schweizerischer Nationalfonds*. Financial support of *CIBA-GEIGY S.A.* and a generous gift of computer time from *SANDOZ S.A.* are gratefully acknowledged.

BIBLIOGRAPHY

[1] *R. W. Hoffmann*, 'Dehydrobenzene and Cycloalkynes', Academic Press, New York 1967.
[2] *P. Millie, L. Praud & J. Serre*, Int. J. of Quantum Chemistry *4*, 187 (1971).
[3] *H. F. Gruetzmacher & J. Lohmann*, Liebigs Ann. Chem. *705*, 81 (1967).
[4] *T. Koopmans*, Physica *1*, 104 (1934); *W. G. Richards*, Int. J. Mass. Spectrom. Ion Physics *2*, 419 (1969).
[5] *L. Praud, P. Millie & G. Berthier*, Theor. chim. Acta *11*, 169 (1968).
[6] *D. R. Stull, E. F. Westrum, jr. & G. O. Sinke*, 'The Chemical Thermodynamics of Organic Compounds', Wiley, New York 1969.
[7] *I. P. Fisher & F. P. Lossing*, J. Amer. chem. Soc. *85*, 1018 (1963).
[8] *C. A. Coulson*, Chem. Soc. Special Publ. Nr. *12*, 85 (1958) [Chem. Abstr. *53*, 463 (1959)].
[9] *T. Yonezawa, H. Konishi & H. Kato*, Bull. chem. Soc. Jap. *41*, 1031 (1968).
[10] *R. Hoffmann, A. Imamura & W. J. Hehre*, J. Amer. chem. Soc. *90*, 1499 (1968).
[11] *M. J. S. Dewar & E. Haselbach*, J. Amer. chem. Soc. *92*, 590 (1970); *N. Bodor, M. J. S. Dewar, A. Harget & E. Haselbach, ibid. 92*, 3854 (1970); *G. Klopman & B. O'Leary*, Fortschr. chem. Forsch. *15*, 445 (1970).
[12] *L. E. Sutton*, 'Table of Interatomic Distances', The Chemical Society, London 1958, 1965.
[13] *H. Kollmar*, Tetrahedron Letters *38*, 3337 (1970).
[14] *R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen & P. Schleyer*, J. Amer. chem. Soc. *91*, 5350 (1969).
[15] *E. Heilbronner & H. Bock*, 'Das HMO-Modell und seine Anwendung', Verlag Chemie, Weinheim 1968.
[16] *R. S. Berry, G. N. Spokes & R. M. Stiles*, J. Amer. chem. Soc. *82*, 5240 (1960); *84*, 3570 (1962).
[17] *D. W. Turner*, 'Molecular Photoelectron Spectroscopy', Wiley-Interscience, New York 1970.
[18] *R. Huisgen, W. Mack & L. Möbius*, Tetrahedron *9*, 29 (1960).
[19] *K. Fukui, T. Yonezawa & H. Shingu*, J. chem. Physics *20*, 722 (1952); *K. Fukui, T. Yonezawa, C. Nagata & H. Shingu, ibid. 22*, 1433 (1954).

[20] *R. B. Woodward & R. Hoffmann*, 'The Conservation of Orbital Symmetry', Verlag Chemie, Weinheim 1970.
[21] *M. J. S. Dewar*, 'The Molecular Orbital Theory of Organic Chemistry', McGraw-Hill, New York 1969.
[22] *G. Porter & J. I. Steinfeld*, J. chem. Soc. [A] *1968*, 877.
[23] *R. W. Carr & W. D. Walters*, J. physic. Chemistry *67*, 1370 (1963).
[24] *J. A. Kerr*, Chem. Rev. *66*, 469 (1966).
[25] *A. S. Rodgers, D. M. Golden & S. W. Benson*, J. Amer. chem. Soc. *89*, 4578 (1967).

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212. Indolo[3,3a,4-*gh*]chinoline und 10a,6a-Iminopropano-indolo[3,3a,4-*gh*]chinoline. Stereospezifische Synthesen und Umlagerungen. Teil I

8. Mitteilung über synthetische Indolverbindungen [1]

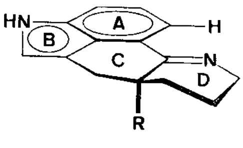
von **André P. Stoll, P. Niklaus** und **F. Troxler**
Pharmazeutisch-chemische Forschungslaboratorien, *Sandoz AG*, Basel

(7. VII. 71)

Summary. The stereospecific cyclization of derivatives of 1-benzyl-5-oxo-1,3,4,5-tetrahydrobenzo[*cd*]indole to *trans*-octahydroindolo[3,3a,4-*gh*]quinolines **3** and **4** is described. The *trans* methyl esters (**4b** and **4c**) were converted with BF_3/CH_3OH to the thermodynamically more stable *cis*-epimers **5**. The structures and stereochemistry of the products, deduced from chemical evidence and analysis of models, are compatible with the NMR. data.

Im Laufe unserer Arbeiten über polycyclische Indolverbindungen beschäftigten wir uns vor einiger Zeit mit dem aus 1,3,4,5-Tetrahydro-benz[*cd*]indol-5-on [2] leicht zugänglichen Dinitril **1**. In dieser und der anschliessenden Mitteilung berichten wir über stereospezifisch verlaufende Cyclisierungen, Epimerisierungen und die stereoelektronisch kontrollierte Ringöffnung einiger Cyclisierungsprodukte; die in dieser Mitteilung besprochenen Umsetzungen sind im Schema 1 zusammengefasst.

1. Cyclisierung von 1 zu 2 und dessen stereospezifische Reduktion zu Verbindungen der allgemeinen Formel 3. – Hydrierung von **1** mit *Raney*-Nickel unter Normalbedingungen in Methanol führt in 51% Ausbeute zu **2**. Der zunächst überraschende Befund, dass dabei nur eine der beiden Nitrilgruppen von **1** reduziert wird, legt den Gedanken nahe, dass diese Reduktion unter Beteiligung der Sauerstofffunktion erfolgt.



$R = CH_2CH_2CN$

Fig. 1. *Räumliche Darstellung von* **2**