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Dedicated to the memory of
Professor Ecaterina Ciorănescu-Nenitzescu (1909–2000)

DIBENZOBICYCLO[2.2.2]OCTANE DERIVATIVES. II.[1] STRUCTURE AND DECOMPOSITION EVIDENCED BY X-RAY ANALYSIS

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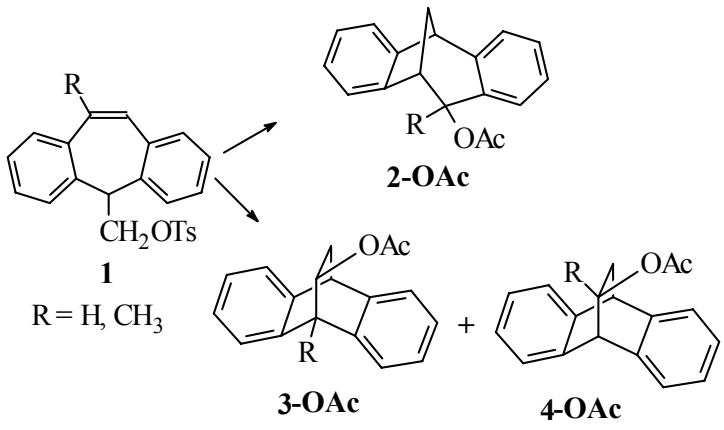
The structure of the previously synthesized *trans*-11,12-dicarbonyl-*N,N'*-(3,5-dimethylpyrazole)-9,10-dihydro-9,10-ethanoanthracene, was doubtlessly confirmed by X-ray analysis. Attempts to prepare a coordination compound with cobalt failed. Instead of the expected compound, the known complex of the 3,5-dimethylpyrazole was obtained, due to ligand decomposition with a dibenzobicyclo[2.2.2]octane diketene molecule elimination. This decomposition reaction is a confirmation of the mechanism recently proposed for explaining the thermal behaviour of the compound. For the first step of the thermal degradation of this dibenzobicyclo[2.2.2]octane derivative, the elimination the same diketene was suggested. The structure of the obtained cobalt coordination compound was also confirmed by X-ray analysis.

INTRODUCTION

The interest of Cioranescu and coworkers,[2,3] for the synthesis and chemistry of dibenzobicyclo[2.2.2]octane derivatives is connected with the study of the solvolytic transformations of a number of dibenzocycloheptene tosylates **1**. The compounds **3**-OAc, with dibenzobicyclo[2.2.2]octane skeleton, have been proposed as the thermodynamically stable π-route products of the performed solvolyses. In kinetic controlled conditions (AcOH + NaOAc) dibenzobicyclo[3.2.1]octane derivatives (**2**-OAc) have been obtained, while in AcOH, without NaOAc as buffer, the compounds with a dibenzobicyclo[2.2.2]octane skeleton (**3**-OAc, **4**-OAc) have been identified as π-route products:



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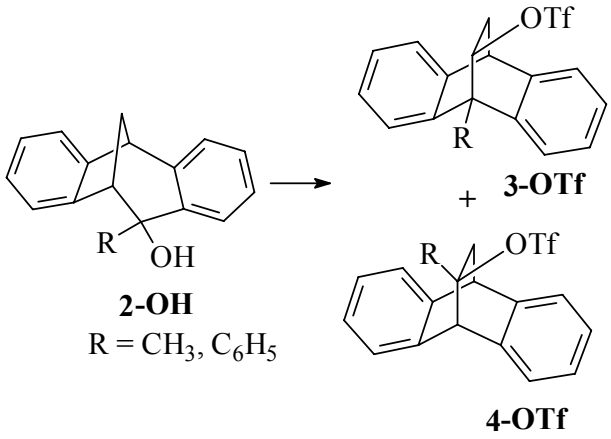
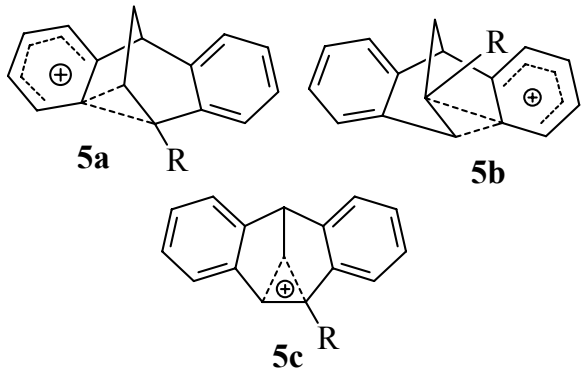
The higher stability of the products similar to **3-**OAc and **4-**OAc was evidenced by their formation from the kinetically controlled products **2-**OH**,** on treatment with trifluoroacetic acid (TfOH): [4]



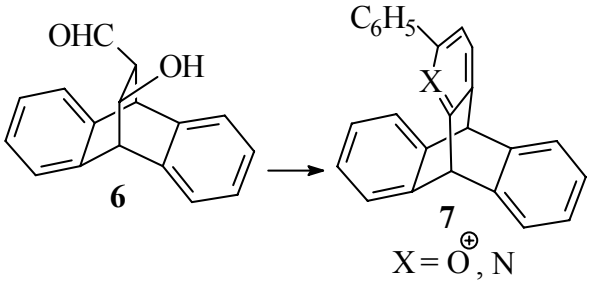
In all these transformations, the carbocations **5a-c** have been proposed as intermediates.[5,6] The formation of phenonium ions (**5a**,**b**) was confirmed by the X-ray structural studies of Pool, White and Woynek.[7]

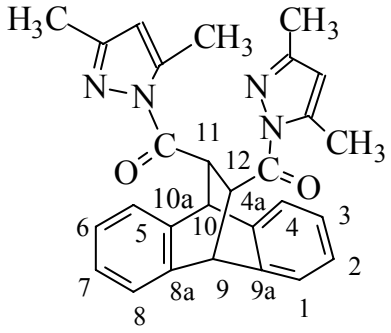


Structures based on the dibenzobicylo[2.2.2] octane skeleton appeared to fulfil the requirements of the pharmacophore and promising results were obtained after the requisite molecules were synthesised. Dibenzobicyclo[2.2.2]derivatives proved to be employed for anticancer therapy,[8] as angiotensin II antagonists,[9] but also as components of regioisomeric chiral stationary phases[10] or as asymmetric catalysts.[11] The study of their stereospecific synthesis seemed also of interest.[12]

Our research group was continuously interested in the subject and other compounds having the same skeleton, such as **6**, have been synthesized, and used either for obtaining complex heterocyclic compounds like triptycene analogues **7,**[13] or as bidentate ligand, for preparing different coordination compounds.[14,15]

Recently, the polycyclic derivative **8,** with a dibenzobicyclo[2.2.2]octane skeleton, have been synthsized.[1]

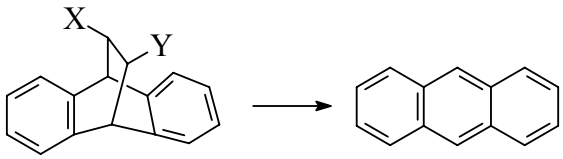




8

The study of this polycyclic compound **8** was of interest based on the structure elements for potential biological activity: the dibenzobicyclo[2.2.2]octane skeleton and two pyrazole moieties.

The presence of pyrazole rings makes the thermal behaviour of compound **8** different from that of the compounds with the same skeleton **6** or **9**.[16] In the first step of the thermal decomposition, of **6** and **9**, the elimination of an anthracene (**10**) molecule by a retro-diene reaction, was evidenced.[17]

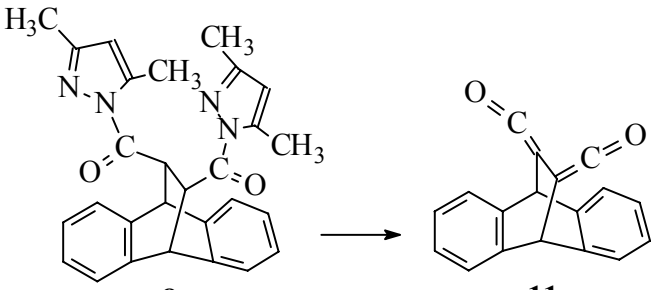


9 **10**

$X = Y = COOCH_3$

$X = Y = CONHNH_2$

The heterocyclic compound **8** decomposed by a different mechanism, an elimination of the diketene **11** being proposed for the first step of its thermal degradation.[16]



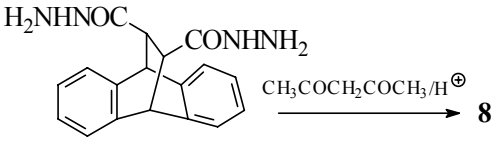
8 **11**

The present paper bring a doubtless confirmation of the compound **8** structure, as well as, a proof for the proposed decomposition mechanism, using as tools the X-ray analyses.

RESULTS AND DISCUSSION

As previously described,[1] the compound **8** was obtained by the condensation of the *trans*-9,10-dihydro-9,10-ethano-anthracene-11,12-dihydrazide (**12**) with acetylacetone in excess and $HClO_4$ in traces, as catalyst.

Its structure was proposed based on IR and NMR spectral data (see experimental). The doubtless confirmation of the structure of this new dibenobicyclo[2.2.2]derivative has came from the X-ray analysis. The structural characterization, performed on a single crystal, showed the following atom distribution, in agreement with the previously proposed structure (see Figure 1).



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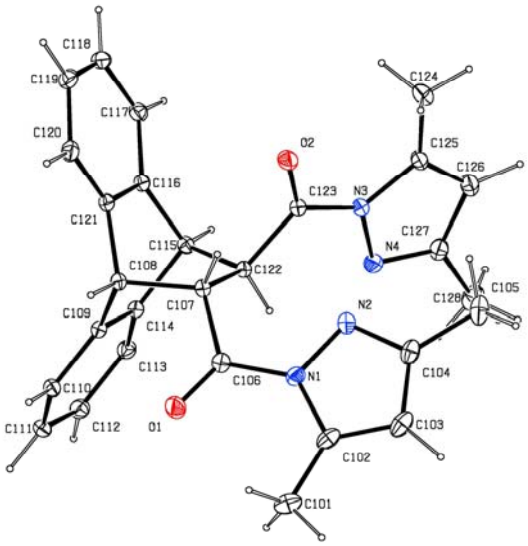


Fig. 1 – Displacement ellipsoid plots (30% probability [18]) of **8** (The H atom are shown with arbitrary radius).

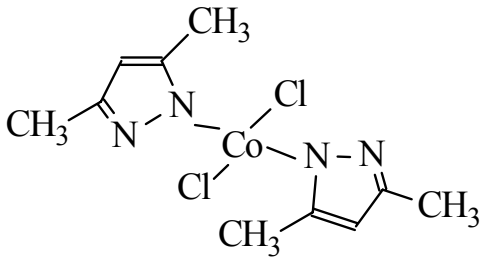
The compound **8** crystallizes in the centrosymmetric space group *P*-1 with two molecules in the unit cell related by inversion. Crystal data for this compound are presented in Table 1:

Table 1

Crystal data for compound **8**

Empirical formula	$C_{28}H_{26}N_4O_2$
Crystal dim. (mm)	0.57 x 0.36 x 0.27
Formula mass	450.53
Crystal system	Triclinic
Space Group	*P*-1
a [Å]	9.3816(7)
b[Å]	10.1397(8)
c [Å]	12.9120(10)
α [°]	76.107(3)
β [°]	80.374(3)
γ [°]	75.079(3)
V [Å^3]	1144.84(15)
Z	2
D [g.cm^{-3}]	1.307
F000	476
μ(Mo-K_α) [mm^{-1}]	0.84
Diffractometer	Bruker Smart CCD
T [K]	110 (2)
θ range	2.40 – 25.00
Refl. collected	11578
Unique refl.	4017
R_{int}	0.0552
Reflections used	4017
Parameters refined	311
R_1	0.0399
wR_2	0.1135
GooF	1.062
Diff. Peak/ hole [e/Å^3]	0.27/ -0.22

The synthesis of the Co(II) coordination compound of **8** was performed according the procedure used for the preparation of the previously described Eu complex.[1] The synthesis started from *trans*-9,10-dihydro-9,10-ethano-anthracene-11,12-dihydrazide (**2**) and acetylacetone, in the presence $CoCl_2 \cdot 6H_2O$ having as catalyst traces of $HClO_4$.The reaction product was not a compound **8** coordination complex, as obtained in the same reaction conditions with the europium salt, but a decomposition product. The analysis of the blue-green crystalline complex, isolated from the reaction mixture, indicates the thermal decomposition of the ligand **8,** previous to complexation, with the elimination of the ketene **11**, the 3,5-dimethylpyrazole complex **14** being obtained.



14

As mentioned before, a similar behaviour was observed during the thermal decomposition of the compound **8**.[16] The 3,5-dimethylpyrazole cobalt complex **14** has been already described in literature,[19] its characteristics corresponding with those of our product. The cobalt atom is tetracoordinated with two 3,5-dimethylpyrazole rings and two chlorine. For proving this assertion the structural data obtained by X-ray analysis are presented.

Crystal data for the coordination compound **14** are presented in **Table 2**.

Such decomposition, at complexation with Co, was not observed in the case of dihydrazide **12**, other polydentate ligand with the same skeleton.[20] The pyrazole moiety change the behaviour of compound **8**, in complexation and thermal decomposition, by comparison with other dibenzobicyclic[2.2.2]octane derivatives studied before. Similar decompositions, with elimination reactions preserving the pyrazole moiety, were evidenced also for other type of compounds.[21] The decomposition of the compound **8** at lower temperature than its thermal decomposition was, most probably, due to the transitional metal catalysis of diketene **11** elimination.

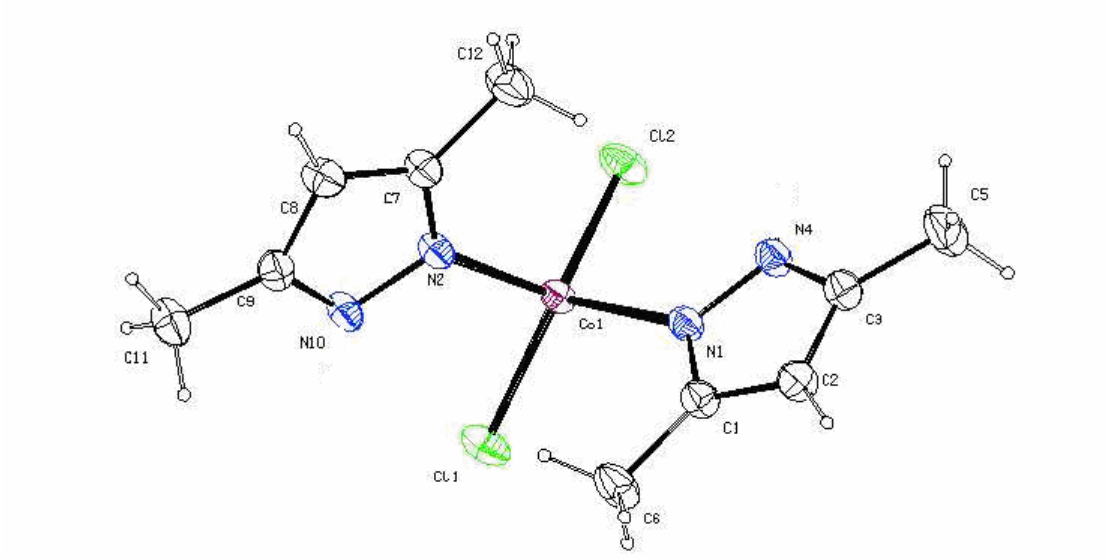


Fig. 2 – Displacement ellipsoid plots (30% probability[18]) of **14**.
(The H atoms are shown with arbitrary radius).

Table 2

Crystal data for the cobalt complex **14**

Empirical formula	$C_{10}H_{16}Cl_2CoN_4$
Crystal size. (mm)	0.85 x 0.27 x 0.14
Formula mass	322.10
Crystal system	Monoclinic
Space Group	C2/c
a [Å]	15.030(5)
b [Å]	8.110(3)
c [Å]	23.898(7)
β [°]	95.409(5)
V [Å^3]	2900.0(15)
Z	8
D [g.cm^{-3}]	1.475
F000	1320
Diffractometer	Bruker Smart CCD
T [K]	110 (2)
θ range [°]	1.71-27.45
Refl. Collected	17785
Indep. refl.	3315
R_{int}	0.0408
R_1	0.0314
wR_2	0.0757
Diff. peak/ hole [e/Å^3]	0.467/ -0.322

EXPERIMENTAL

The IR spectra have been recorded with a K. Zeiss Jena U 20 spectrophotometer and NMR spectra with a Gemeni 300-Varian apparatus (with internal TMS).

***trans*-11,12-Dicarbonyl-*N,N'*-(3,5-dimethylpyrazole)-9,10-dihydro-9,10-ethanoanthracene (8)**

It is a white solid (m.p. 233-4°C) obtained by titration with diethylether of the compound obtained from the one-pot condensation of *trans*-9,10-dihydro-9,10-ethano-anthracene-11,12-dihydrazide (**12**) and acetylacetone (**13**) in excess and $HClO_4$ as catalyst.[1]

Elemental analysis for $C_{28}H_{26}N_4O_2$ Found (calculated): C 73,75 % (74.65 %), H 5,64 % (5.82 %), N 11,39 % (12,44%).

IR Spectrum(CCl_4, cm^{-1}): 701 w, 755 s, 768 m, 913 w, 939 w, 963 m, 1248 w, 1325 vs, 1342 s, 1381 vs, 1410 m, 1582 m, 1720 $vs_{(C=O)}$, 2907 w, 2971 w, 3024 w, 3070 w, 3101 w.

^{13}C NMR Spectrum ($CDCl_3$, ppm): 172.61 (C=O, C_{13},C_{14}), 151.34 (C=N,$C_{3'}$,$C_{3''}$), 144.0 (C-N,$C_{5'}$,$C_{5''}$), 142.48 (C_{8a},C_{8b}); 140.81 (C_{4a},C_{4b}); 126.19 (C_2,C_6); 126.05 (C_3,C_7); 125.44 (C_4,C_8); 123.51 (C_1,C_5); 52.32 (CH,$C_{4'}$,$C_{4''}$); 48.87 (C_9,C_{10}); 46.92 (C_{11},C_{12}), 14.47 (CH_3), 13.45 (CH_3).

^{1}H NMR Spectrum ($CDCl_3$, ppm): 7.38 m (H_1,H_5), 7.28 m (H_4,H_8), 7.14 m (H_3,H_7), 7.11 m (H_2,H_6), 5.86 s (CH), 4.78 s (H_9,H_{10}), 4.47 s (H_{11},H_{12}), 2.42 s (CH_3), 2.00 s (CH_3).

Complex 14 synthesis

An ethanolic solution of the *trans*-9,10-dihydro-9,10-ethano-anthracene-11,12-dihydrazide (**12**), acetylacetone (**13**) and $CoCl_2 \cdot 6H_2O$, in molar ratio 2:2:1, was refluxed for 10 h in the presence of catalytic amount of $HClO_4$. After evaporation of the solvent a blue-green solid was obtained.

The same compound **14** was obtained on treatment of compound **8** with $CoCl_2 \cdot 6H_2O$, molar ratio 1/1 in ethanol after 10 h of reflux.

Elemental analysis Found (calculated): C 58.12% (57.73 %), H 5.24% (4.88%), N 10.34 % (9.62%), Cl 12.52% (12.19%), Co 9.64% (10.10%).

IR Spectrum(CCl_4, cm^{-1}): 761 s, 960 w, 1019 m, 1114 m, 1197 s, 1264 vs, 1434 m, 1571 s, 2852 w, 2951 m, 3145 w, 3318 m.

X-ray Structure Determination

For intensity data collection the single crystals were mounted on glass fibers and placed directly in a cold stream of dinitrogen. Crystal data, parameters in data collection and convergence results are listed in Tables 1 and 2. Data collection were performed at 110 K with a Bruker Smart APEX CCD (Mo-K_α radiation, λ= 0.71073 Å, graphite monochromator) area detector. The unit cell parameters were obtained by the least-squares refinement of up to 999 reflections. The structures were solved by direct methods (SHELXS-97)[22] and refined by full matrix least-squares procedures based on F^2 with all measured reflections (SHELXL-97).[23] The SADABS[24] program was used for absorption correction of the structures. Non-hydrogen atoms were refined anisotropically and H atoms were introduced in their idealized positions and refined using a riding model.

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC- 279625 and 713909 for **8** and **14** respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: int. code + (1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk; web, www: http://www.ccdc.cam.ac.uk).

CONCLUSIONS

The structure of the previously synthesized *trans*-11,12-dicarbonyl-*N,N'*-(3,5-dimethylpyrazole)-9,10-dihydro-9,10-ethanoanthracene (**8**) was confirmed by X-ray structural analysis. Attempts to synthesize a Co(II)

complex of compound **8** failed, the known complex of 3,5-dimethylpyrazole being obtained instead, complex also evidenced by the X-ray spectral data. This behaviour is a doubtless confirmation of the mechanism previously proposed for the thermal decomposition of the compound **8**.

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