Tetrahedron Letters 52 (2011) 1854–1857

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Kinetic control wins out over thermodynamic control in Friedel–Crafts acyl rearrangements

Tahani Mala'bi, Sergey Pogodin, Israel Agranat *

Organic Chemistry, Institute of Chemistry, The Hebrew University of Jerusalem, Philadelphia Bldg, #201/205, Edmond J. Safra Campus, Jerusalem 91904, Israel

ARTICLE INFO

Article history:
Received 28 December 2010
Revised 20 January 2011
Accepted 4 February 2011
Available online 4 March 2011

Keywords:
Diacetylanthracenes
Polyphosphoric acid
Reversibility
Rearrangement mechanism
DFT calculations

ABSTRACT

1,5-, 1,8- and 9,10-diacetylanthracenes undergo Friedel–Crafts acyl rearrangements in polyphosphoric acid at 130–150 °C to give 3-methylbenz[*de*]anthracen-1-one via the kinetically-controlled 1,9-diacetylanthracene. The rearrangement mechanism is supported by DFT calculations of diacetylanthracenes, their σ-complexes, *O*-protonates, and *O*,*O*-diprotonates. The importance of kinetic control versus thermodynamic control in Friedel–Crafts acyl rearrangements is highlighted. Certain features of reversibility are also suggested.

Friedel–Crafts acylation, in contrast to Friedel–Crafts alkylation, is usually considered an irreversible process, free of rearrangements and isomerizations.[1–3] However, if the acyl group is tilted out of the plane of the aromatic ring by the neighboring bulky group(s), the resonance stabilization is reduced and the pattern of irreversibility of the Friedel–Crafts acylation may be challenged, allowing deacylations, transacylations, and acyl rearrangements.[4–6] The concept of reversibility in Friedel–Crafts acylation was put forward in 1955 by Gore, who proposed that 'the Friedel–Crafts acylation reactions of reactive hydrocarbons is a reversible process'.[7,8] The incursion of reversibility in the Friedel–Crafts acylation was revealed in the benzoylation of naphthalene in polyphosphoric acid (PPA) at elevated temperatures.[9] Under classical Friedel–Crafts acylation conditions (e.g., $AlCl_3$ and a trace of H_2O), the pattern of irreversibility (e.g., in the naphthalene series) has been highlighted.[6,8,10,11] The existing experimental evidence in support of the true reversibility of Friedel–Crafts acylation is limited.[12–17] Notable cases are the report by Balaban on the reversibility of Friedel–Crafts acetylation of olefins to β-chloroketones,[12–14] the report by Effenberger of the retro-Fries rearrangement of phenyl benzoates (CF_3SO_3H, 170 °C)[15] and the reversible $Ar-S_E$ aroylation of naphthalene derivatives.[17] Complete reversibility of Friedel–Crafts acylation was established in the intramolecular *para* ⇌ *ortho* acyl rearrangements of fluorofluorenones in PPA.[18] Friedel–Crafts acylation can be adjusted to give a kinetically controlled ketone or a thermodynamically controlled ketone.[4] Acyl rearrangements and reversibility in Friedel–Crafts acylations have been associated with thermodynamic control.[5,9,18] The contributions of kinetic control versus thermodynamic control in Friedel–Crafts acyl rearrangements remain an open question, in spite of the rich chemistry of the Friedel–Crafts acylation.

Aspects of reversibility and acyl rearrangements of mono-acetylanthracenes and mono-acetylphenanthrenes in PPA have been reported, but complete reversibility has not been realized.[19,20] The complexity of the Friedel–Crafts acetylation of anthracene is enhanced by diacetylation. Indeed, the disproportionations of 9-acetylanthracene into 1,5-diacetylanthracene and 1,8-diacetylanthracene in an ionic liquid system have been described.[16] The study of the mutual Friedel–Crafts acyl rearrangements of diacetylanthracenes with special emphasis on kinetic versus thermodynamic control seemed an attractive proposition. We provide here experimental and theoretical evidence indicating the importance of kinetic control in the Friedel–Crafts acyl rearrangements in the diacetylanthracene series. We report that surprisingly, the Friedel–Crafts acyl rearrangements of 1,5-diacetylanthracene (**1,5-Ac$_2$AN**), 1,8-diacetylanthracene (**1,8-Ac$_2$AN**) and 9,10-diacetylanthracene (**9,10-Ac$_2$AN**) in PPA gave 3-methylbenz[*de*]anthracen-1-one (**1**) via the putative kinetically controlled intermediate, 1,9-diacetylanthracene (**1,9-Ac$_2$AN**).

1,5-Ac$_2$AN,[21,22] **1,8-Ac$_2$AN**[23] and **9,10-Ac$_2$AN**[24] were each subjected to PPA at 130–150 °C for 1–4 h. The results are summarized in Table 1. The constitution of the crude products was established by ^{1}H NMR spectroscopy. The constitutional isomers **1,5-Ac$_2$AN**,

* Corresponding author.
E-mail address: isria@vms.huji.ac.il (I. Agranat).

0040-4039/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2011.02.026

Table 1
The products of the rearrangements of diacetylanthracenes

Substrate	*T*	*t*	Products (% relative yield)							
***m,n*-**			*m*-AcAN			*m,n*-Ac_2AN				
Ac_2AN	(°C)	(h)	1	2	9	1,5	1,8	9,10	**1**	AN
1,5	140	1	0	26	0	14	16	0	44	0
1,5	150	1	0	30	0	15	5	0	50	0
1,5	150	3	0	0	0	5	2	0	93	0
1,8	130	3	0	11	0	0	24	0	65	0
1,8	130	4	0	0	0	0	20	0	80	0
1,8	140	1	0	17	0	0	21	0	62	0
1,8	150	3	0	9	0	0	12	0	79	0
9,10	150	1	3	8	0	0	0	50	8	31
9,10	150	3	0	5	0	0	0	18	0	77

1,8-Ac_2AN, and **9,10-Ac_2AN**, the constitutional isomers 1-acetylanthracene (**1-AcAN**), 2-acetylanthracene (**2-AcAN**), and 9-acetylanthracene (**9-AcAN**) and anthracene (**AN**) were distinguished by the ^{1}H NMR chemical shifts of the methyl groups, by the low-field chemical shifts of H^9 and H^{10} (singlets) and the chemical shifts of the protons *ortho* to the carbonyl group(s) (H^1 and/or H^2) (Table 2).

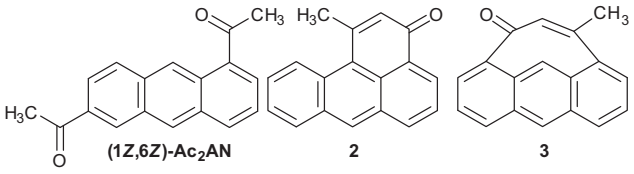
The major rearrangement product of the reactions of **1,5-Ac_2AN** and **1,8-Ac_2AN** in PPA was **1**. In both cases, **2-Ac_2AN** was also formed. **1,5-Ac_2AN** also rearranged into **1,8-Ac_2AN** (probably via **1-AcAN**), while **1,8-Ac_2AN** did not rearrange into **1,5-Ac_2AN**. Interestingly, **1** was also formed from **9,10-Ac_2AN**. The latter also underwent a rearrangement into **2-AcAN** and deacetylation to give **AN** as the major product. 1,6-Diacetylanthracene[25] was not identified among the products of the reactions.

Preparative rearrangement of **1,5-Ac_2AN** in PPA (at 150 °C) for three hours gave **1** in 25% yield. The structure of **1** was verified by 2D ^{1}H NMR and ^{13}C NMR spectroscopy. The very low field double doublet of the bay-region H^{11} at 10.16 ppm (see Table 2) due to the diamagnetic anisotropy effect of the neighboring C^1=O is striking. The chemical shifts of the ethylenic H^2 and of the CH_3 group at 6.75 and 2.57 ppm, respectively, are also noteworthy. Compound **1** could be distinguished from its constitutional isomer, 1-methylbenz[*de*]anthracen-3-one (**2**) by the NOE between the CH_3 and H^4 (8.01 ppm, dd) in **1**, while no NOE was observed between CH_3 and H^{11} (which would be expected for **2**). The structure of the highly strained 4-methylcycloocta[*defg*]anthracen-1-one (**3**) was ruled out by the absence of a singlet due to H^{10}. (Also, H^{11} of **3** which is not located in a bay region would not have been expected to be so highly deshielded as H^{11} of **1**). The DFT calculations also show that **1** is more stable than **2** and **3**: ΔG_{298} = 0.0 (**1**), 31.35 (**2**), 346.39 (**3**) kJ/mol.

Table 2
^{1}H NMR chemical shifts (500 MHz, $CDCl_3$, ppm) of characteristic protons in mono- and diacetylanthracenes, and in **1**[a]

	CH_3	H^9	H^{10}	H^1	H^2
1-AcAN	2.81, s	9.48, s	8.44, s	—	8.01, d (7.0)
2-AcAN	2.76, s	8.57, s	8.43, s	8.65, s	—
9-AcAN	2.82, s	—	8.47, s	7.86, d (8.5)	7.47–7.55, m
1,5-Ac_2AN	2.82 s	9.57, s	9.57, s	—	8.08, d (7.0, 1.0)
1,8-Ac_2AN	2.83, s	10.17, s	8.47, s	—	8.14, d (8.5)
9,10-Ac_2AN	2.81, s	—	—	7.84–7.88, m	7.53–7.57, m
1,6-Ac_2AN	2.79, s 2.73, s	9.46 s	8.52, s	8.57,[b] s	8.04, d (7.0)
1	2.57, d (1.0)	—	8.73,[c] s	10.16,[d] dd, (9.0, 1.0)	8.01,[e] dd, (7.3, 1.0)

[a] Coupling constants (*J*, Hz) are given in parentheses.
[b] H^5.
[c] H^7.
[d] H^{11}.
[e] H^4.



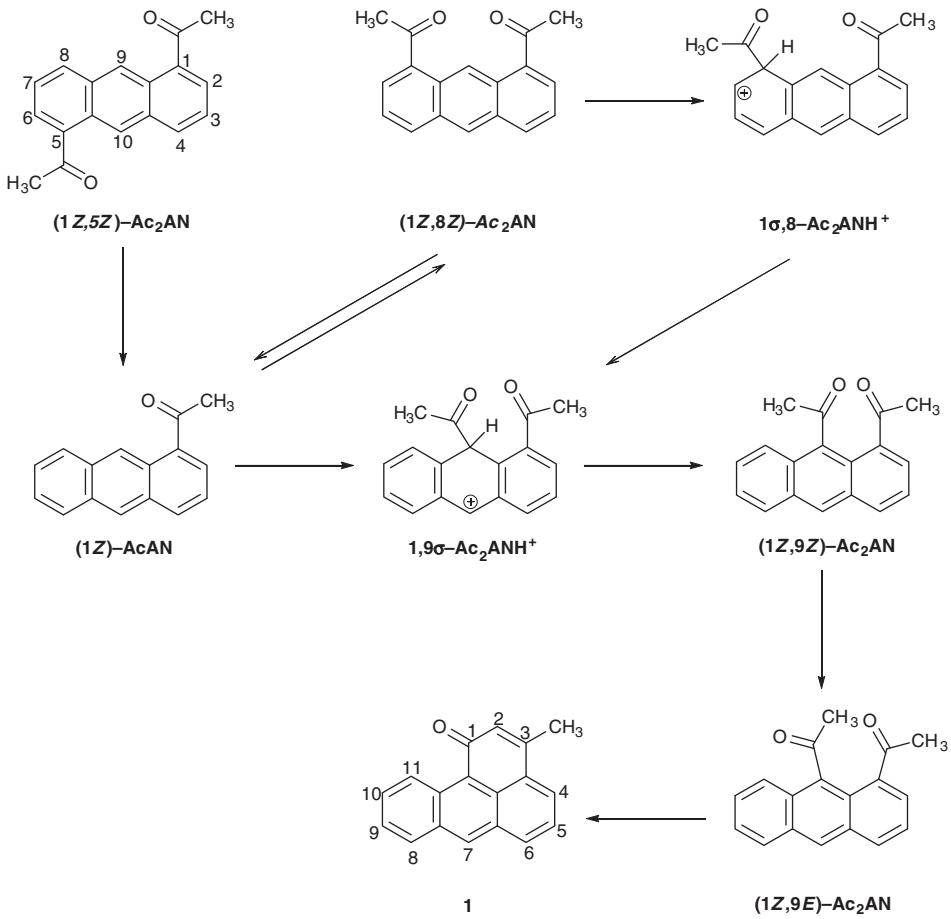
A plausible mechanism for the rearrangements of **1,5-Ac_2AN** and **1,8-Ac_2AN** into **1** is presented in Scheme 1. The pivotal step in this mechanism is the formation of **1,9-Ac_2AN** as an intermediate. **1,5-Ac_2AN** and **1,8-Ac_2AN** each undergoes deacetylation to give **1-AcAN**, followed by reacetylation to give the kinetically controlled **1,9-Ac_2AN** (vide infra). The latter can also be formed by a direct acyl rearrangement of **1,8-Ac_2AN**: **1,8-Ac_2AN** → **1,8σ-Ac_2ANH^{+1}** → **1,9σ-Ac_2ANH^{+1}** → **1,9-Ac_2AN**.

The rearrangement of the latter into **1** requires a (1*Z*,9*Z*) → (1*Z*,9*E*) diastereomerization.[26] Figure 1 depicts the DFT-calculated transition state for the rearrangement of **1,8σ-Ac_2AN** into **1,9σ-Ac_2AN** (energy barrier $\Delta\Delta G^{\ddagger}_{298}$ = 35.9 kJ/mol, at B3LYP/6-31G(d)). The **1,9-Ac_2AN** intermediate then undergoes an acid-catalyzed irreversible intramolecular aldol condensation to give **1**. **1,9-Ac_2AN** may also be an intermediate in the rearrangement of **9,10-Ac_2AN** into **1** (see Scheme SD1, Supplementary data). The acyl rearrangement mechanism also suggests certain features of reversibility: **1,5-Ac_2AN** → **1-AcAN** ⇌ **1,8-Ac_2AN**. The reported formation of **1** from anthracene and diketene (HF, −30 to +60 °C)[27] may be rationalized by an initial Friedel–Crafts acylation at C^9, followed by an intramolecular alkylation at C^1 and dehydration.

The proposed mechanism is supported by the results of DFT calculations of the diacetylanthracenes, their *O*-protonates, their *O*,*O*-diprotonates and their σ-complexes at B3LYP/6-31G(d) (Tables SD1–SD4, Supplementary data). Recently, a computational model for predicting the site for electrophilic aromatic substitution was reported.[28] The model was based on DFT calculations of the relative stabilities of the σ-complex intermediates and was applied (inter alia) to Lewis acid protonated Friedel–Crafts acylations. Our calculations (see Supplementary data for the details) give the following orders of relative free energies (ΔG_{298}, kJ/mol) of **1,5-Ac_2AN**, **1,8-Ac_2AN**, **1,9-Ac_2AN**, **1,10-Ac_2AN**, and **9,10-Ac_2AN** in each series:

- σ-complexes of diacetylanthracenes: ΔG_{298} = 0.0 (**1,9σ-Ac_2ANH^{+1}**), 5.68 (**1,10σ-Ac_2ANH^{+1}**), 22.29 (**9σ,10-Ac_2ANH^{+1}**), 37.54 (**1σ,5-Ac_2ANH^{+1}**), 38.26 (**1σ,8-Ac_2ANH^{+1}**), 58.29 (**1σ,9-Ac_2ANH^{+1}**), 66.99 (**1σ,10-Ac_2ANH^{+1}**).
- *O*-protonated diacetylanthracene monocations: ΔG_{298} = 0.0 [(**1*Z*,8*Z***)-**1*H*-Ac_2ANH^{+1}**], 1.79 [(**1*Z*,5*Z***)-**1*H*-Ac_2ANH^{+1}**], 30.01 [(**1*Z*,10*E***)-**10*H*-Ac_2ANH^{+1}**], 32.34 [(**1*Z*,10*Z***)-**1*H*-Ac_2ANH^{+1}**], 51.50 [(**1*E*,9*E***)-**9*H*-Ac_2ANH^{+1}**],[29] 53.54 [(**1*E*,9*E***)-**1*H*-Ac_2ANH^{+1}**], 55.31 [(**9*E*,10*E***)-**9*H*-Ac_2ANH^{+1}**].
- *O*,*O*-protonated diacetylanthracene dications: ΔG_{298} = 0.0 [(**1*Z*,5*Z***)-$Ac_2ANH_2^{+2}$], 11.24 [(**1*Z*,8*Z***)-$Ac_2ANH_2^{+2}$], 71.39 [(**1*Z*,10*Z***)-$Ac_2ANH_2^{+2}$], 88.44 [(**1*Z*,9*Z***)-$Ac_2ANH_2^{+2}$], 151.52 [(**9*E*,10*E***)-$Ac_2ANH_2^{+2}$].
- diacetylanthracenes: ΔG_{298} = 0.0 [(**1*Z*,5*Z***)-**Ac_2AN**], 11.20 [(**1*Z*,8*Z***)-**Ac_2AN**], 22.74 [(**1*Z*,10*Z***)-**Ac_2AN**], 42.63 [(**1*Z*,9*Z***)-**Ac_2AN**], 43.87 [(**9*E*,10*E***)-**Ac_2AN**].

Figure 2 depicts the relative energies of the most stable conformations of each of the diacetylanthracene species. The B3LYP/6-31G(d) calculated order of stabilities of the σ-complexes of diacetylanthracenes is **1,9σ-Ac_2ANH^{+1}** > **1,10σ-Ac_2ANH^{+1}** > **9σ,10-Ac_2ANH^{+1}** > **1σ,5-Ac_2ANH^{+1}** > **1σ,8-Ac_2ANH^{+1}** > **1σ,9-Ac_2ANH^{+1}** > **1σ,10-Ac_2ANH^{+1}**. According to the Hammond-Leffler postulate,[30] the



Scheme 1. The mechanism of Friedel–Crafts rearrangement of **1,5-Ac$_2$AN** and **1,8-Ac$_2$AN** leading to **1**.

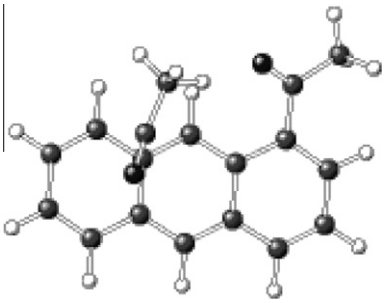


Figure 1. The transition state for **1,8σ-Ac$_2$AN** → **1,9σ-Ac$_2$AN** rearrangement.

relative energies of the transition states leading to the σ-complexes resemble those of the σ-complexes: $\Delta G^{\ddagger}_{298}$ (**1,9σ-Ac$_2$ANH^{+1}**) < $\Delta G^{\ddagger}_{298}$ (**1,10σ-Ac$_2$ANH^{+1}**) < $\Delta G^{\ddagger}_{298}$ (**1σ,5-Ac$_2$ANH^{+1}**) < $\Delta G^{\ddagger}_{298}$ (**1σ,8-Ac$_2$ANH^{+1}**) < $\Delta G^{\ddagger}_{298}$ (**1σ,9-Ac$_2$ANH^{+1}**) < $\Delta G^{\ddagger}_{298}$ (**1σ,10-Ac$_2$ANH^{+1}**). Thus, the DFT calculations predict that **1,9-Ac$_2$AN** is the kinetically controlled product. Among the diacetylanthracenes, only **1,9-Ac$_2$AN** can undergo an irreversible intramolecular aldol condensation to give **1**. By contrast, the calculations show that among the relevant diacetylanthracenes **1,5-Ac$_2$AN**, **1,8-Ac$_2$AN**, **1,9-Ac$_2$AN**, **1,10-Ac$_2$AN**, and **9,10-Ac$_2$AN**, **1,5-Ac$_2$AN** is the most stable. Among *O*-protonated diacetylanthracenes, **1,5-Ac$_2$ANH^{+1}** and **1,8-Ac$_2$ANH^{+1}** are the most stable. Thus they could have qualified as the thermodynamically controlled diacetylanthracenes. The results indicate that the kinetically controlled **1,9-Ac$_2$AN** eventually cyclizes irreversibly to **1**. The Friedel–Crafts acetylation of anthracene under classical conditions

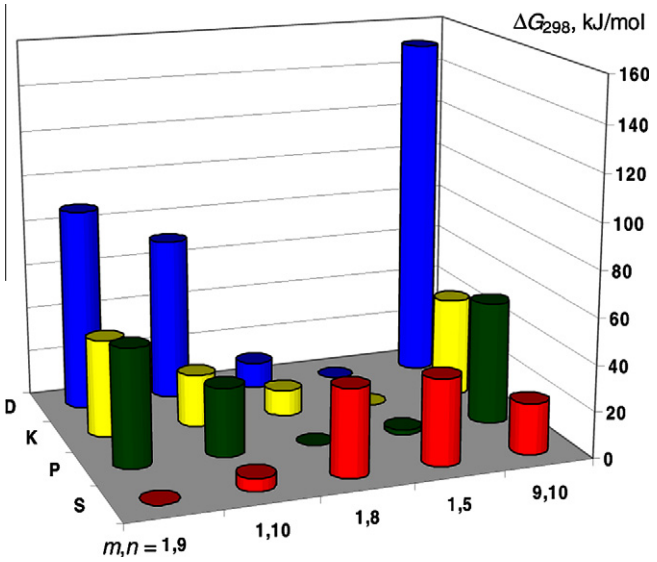


Figure 2. Relative energies (ΔG_{298}) of *m,n*-diacetylanthracene species: σ-complexes (**S**), *O*-protonated diacetylanthracenes (**P**), diacetylanthracenes(**K**), and *O,O*-diprotonated diacetylanthracenes (**D**).

(**AN**, AcCl/AlCl$_3$, CH$_2$Cl$_2$) yielded **1,5-Ac$_2$AN** (30–35 °C, 2 h) and **1,8-Ac$_2$AN** (23 °C, 14 h), but not **1**. Evidently, the σ-complex of **1,9-Ac$_2$AN**, the precursor of **1**, could not have been formed due to a steric hindrance during complexation with AlCl$_3$.

In conclusion, the formation of **1** via **1,9-Ac$_2$AN** in the Friedel–Crafts acyl rearrangements of diacetylanthracenes in PPA (vide supra) supports the contention that in these reactions, kinetic control wins out over thermodynamic control. It remains to be seen whether this conclusion applies to other polycyclic aromatic ketones (PAKs) and whether intermolecularity and/or intramolecularity are essential ingredients of kinetic control in Friedel–Crafts acyl rearrangements of PAKs (Agranat–Gore rearrangement[19]).

Experimental

In a 150 mL round-bottomed flask with a magnetic stirrer and anhydrous argon atmosphere, PPA (133 g) was added; after stirring for a few minutes at 150 °C, **1,5-Ac$_2$AN** (1.0 g, 3.8 mmol) was added. The mixture was stirred at 150 °C for 3 h, and then poured into a mixture of ice and water (500 mL) and stirred overnight. The products were extracted with CH_2Cl_2 (4 × 50 mL), washed with saturated $NaHCO_3$ solution (2 × 50 mL) and H_2O (2 × 50 mL), and dried over $MgSO_4$. The organic solvent was evaporated in vacuo to give a crude mixture of **1** and **1,5-Ac$_2$AN** in an 85:15 ratio. The crude product was purified by repeated column chromatography on silica gel 60, using petroleum ether (40–60 °C)–EtOAc as eluent, from 98:2 to 80:20, followed by recrystallization from EtOAc. Compound **1** was obtained as red crystals, mp 193 °C (lit., mp 182 °C[27]) in 25% yield; MS, m/z = 244 ($^{12}C_{18}H_{12}O$); IR, 1635 cm^{-1} (C=O); UV/Vis ($CHCl_3$, 1.4 × 10^{-4} M nm): 489 sh (ε 7500), 462 (ε 8350), 442 sh, 370 (ε 7700), 354 sh (ε 7400), 269 (ε 26000), 241 (ε 25800) (lit., 462, 488 sh[27]). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 10.16 (dd, J_1 = 9.0 Hz, J_2 = 1.0 Hz, 1H, H^{11}), 8.73 (s, 1H, H^7), 8.13 (d, J = 8.0 Hz, 1H, H^6), 8.07 (dt, J_1 = 8.3 Hz, J_2 = 0.5 Hz, J_3 = 1.0 Hz, 1H, H^8), 8.01 (dd, J_1 = 7.2, J_2 = 1.0 Hz, 1H, H^4), 7.83 (ddd, J_1 = 9.0 Hz, J_2 = 7.0 Hz, J_3 = 1.5 Hz, 1H, H^{10}), 7.61 (ddd, J_1 = 8.3 Hz, J_2 = 6.8 Hz, J_3 = 1.0 Hz, 1H, H^9), 7.57 (dd, J_1 = 8.5 Hz, J_2 = 7.0 Hz, 1H, H^5), 6.75 (d, J = 1.0 Hz, 1H, H^2), 2.57 (d, J = 1.0 Hz, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ = 187.8 (C^1=O), 145.4 (C^3), 137.4 (C^7), 133.4 (C^{11a}), 133.1 (C^6), 132.2 (C^{7a}), 131.7 (C^{10}), 130.9 (C^2), 129.8 (C^4), 129.7 (C^{3a}), 129.6 (C^{6a}), 129.3 (C^8), 128.3 (C^{11c}), 127.8 (C^{11}), 126.3 (C^9), 125.0 (C^5), 122.7 (C^{11b}), 19.3 (CH_3).

Supplementary data

Supplementary data (^{1}H NMR spectrum of **1**; total energies, relative energies, and geometries of the diacetylanthracenes, their *O*-protonates, their *O*,*O*-diprotonates and their σ-complexes) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.02.026.

References and notes

1. *Friedel–Crafts Chemistry*; Olah, G. A., Ed.; Wiley-Interscience: New York, 1973. p 102.
2. *Comprehensive Organic Name Reactions and Reagents*; Wang, Z., Ed.Friedel-Crafts Acylation; Wiley, 2009; Vol. 1, pp 1126–1130. Chapter 248.
3. Norman, R. O. C.; Taylor, R. *Electrophilic Substitution in Benzenoid Compounds*; Elsevier: London, 1965. pp 174–182.
4. Buehler, C. A.; Pearson, D. E. *Survey of Organic Synthesis*; Wiley-Interscience: New York, 1970. p. 653.
5. Pearson, D. E.; Buehler, C. A. *Synthesis* **1971**, 455–477.
6. Gore, P. H. *Chem. Ind.* **1974**, *18*, 727–731.
7. Gore, P. H. *Chem. Rev.* **1955**, *55*, 229–281.
8. Gore, P. H., Ed.Friedel–Crafts and Related Reactions; Olah, G. A., Ed.; Wiley-Interscience: New York, 1964; Vol. 3, pp 1–381 (part 1).
9. Agranat, I.; Shih, Y.-S.; Bentor, Y. *J. Am. Chem. Soc.* **1974**, *96*, 1259–1260.
10. Andreou, A. D.; Gore, P. H.; Morris, D. F. C. *J. Chem. Soc. Chem. Commun.* **1978**, 271–272.
11. Dowdy, D.; Gore, P. H.; Waters, D. N. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1149–1159.
12. Frangopol, M.; Genunche, A.; Frangopol, P. T.; Balaban, A. T. *Tetrahedron* **1964**, *20*, 1881–1888.
13. Balaban, A.T. In *Omagiu Acad. Prof. Raluca Ripan,*; Dragulesea, C., Ed.; Editura Academiei Republicii Socialiste Romania: Bucharest, 1966.
14. Nenitzescu, C. D.; Balaban, A. T. In *Friedel–Crafts and Related Reactions*; Olah, G. A., Ed.; Wiley-Interscience: New York, 1964; vol. 3, pp 1033–1152 (part 2).
15. Effenberger, F.; Klenk, H.; Reiter, P. L. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 775–776.
16. Adams, C. J.; Earle, M. J.; Roberts, G.; Seddon, K. R. *Chem. Commun.* **1998**, 2097–2098.
17. Okamoto, A.; Yonezawa, N. *Chem. Lett.* **2009**, *38*, 914–915.
18. Agranat, I.; Bentor, Y.; Shih, Y.-S. *J. Am. Chem. Soc.* **1977**, *99*, 7068–7070.
19. Mala'bi, T.; Cohen, S.; Pogodin, S.; Agranat, I. *Lett. Org. Chem.* **2009**, *6*, 237–241.
20. Levy, L.; Pogodin, S.; Cohen, S.; Agranat, I. *Lett. Org. Chem.* **2007**, *4*, 314–318.
21. Bassilios, H. F.; Shawky, M.; Salem, A. Y. *Recl. Trav. Chim. Pays-Bas* **1962**, *81*, 679–682.
22. Bassilios, H. F.; Shawky, M.; Salem, A. Y. *Recl. Trav. Chim. Pays-Bas* **1963**, *82*, 298–301.
23. Sarobe, M.; Jenneskens, L. W. *J. Org. Chem.* **1997**, *62*, 8247–8250.
24. Duerr, B. F.; Chung, Y.-S.; Czarnik, A. W. *J. Org. Chem.* **1988**, *53*, 2120–2122.
25. Gore, P. H.; Thadani, C. K. *J. Chem. Soc. C* **1966**, 1729–1733.
26. (*E*) and (*Z*) are the stereodescriptors applied to the acetylanthracene and diacetylanthracene structures with a fractional bond order of the bond between the carbonyl carbon and the aromatic carbon.
27. Compound **1** has been described in the patent literature: DE 2,262,857 (A1) (27.06.1974); Eiglmeier, K. *Chem. Abstr.* **1974**, *81*, 105112p (Accession Number 1974:505112).; GB 1,395,279 (A) (21.05.1975); Eiglmeyer, K. *Chem. Abstr.* **1974**, *81*, 120343h (Accession Number 1974:520343).; US 3,865,879 (A) (11.02.1975); Eiglmeier, K. *Chem. Abstr.* **1973**, *79*, 137936k (Accession Number 1973:537936).
28. Liljenberg, M.; Brinck, T.; Herschend, B.; Rein, T.; Rockwell, G.; Svensson, M. *J. Org. Chem.* **2010**, *75*, 4696–4705.
29. The calculations of the (*Z*,*Z*) and (*E*,*Z*) conformations of **1*H*,9-Ac$_2$AN**$^{+1}$ lead to a hemiketal, see Supplementary data.
30. Muller, P. *Glossary of Terms Used in Physical Organic Chemistry (IUPAC Recommendations 1994)*, *Pure Appl. Chem.* **1994**, *66*, 1077–1184.