

Vitrigens. III [3]

Low Molecular-Weight Glassy Fulvenes

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Abstract. Fulvenes **3** were synthesized from 1,2,3,4-tetra-phenylcyclopenta-1,3-diene (**1**) and different aldehydes **2**.

They are glass-forming materials with well-defined glass-transition temperatures between 74°C and 120°C.

Compared with crystals, amorphous materials are attractive as functional materials due to excellent processability, transparency, isotropic properties, and no grain boundaries. Not only polymers but also molecularly doped polymer systems have received attention for academic and practical interest. A relatively new class of glassy materials are low molecular weight compounds that are able to form stable glasses with glass temperatures above room temperature [1–4]. These materials are of interest for applications as photoconductors or light-emitting devices (LED's) [5, 6]. To date only a limited number of such stable organic glasses is known.

Considerations based on incremental methods [7] or on free volume concepts [8] suggest that bulky molecular systems should exhibit a tendency towards high glass transition temperatures. Such an approach also allows the introduction of functions directly into the glass forming compounds. We have synthesized a series of bulky oddshaped fulvenes **3** from 1,2,3,4-tetra-phenylcyclopenta-1,3-diene (**1**) and various aldehydes **2** with sodium methanolate as base under water separation (Scheme 1, Table 1).

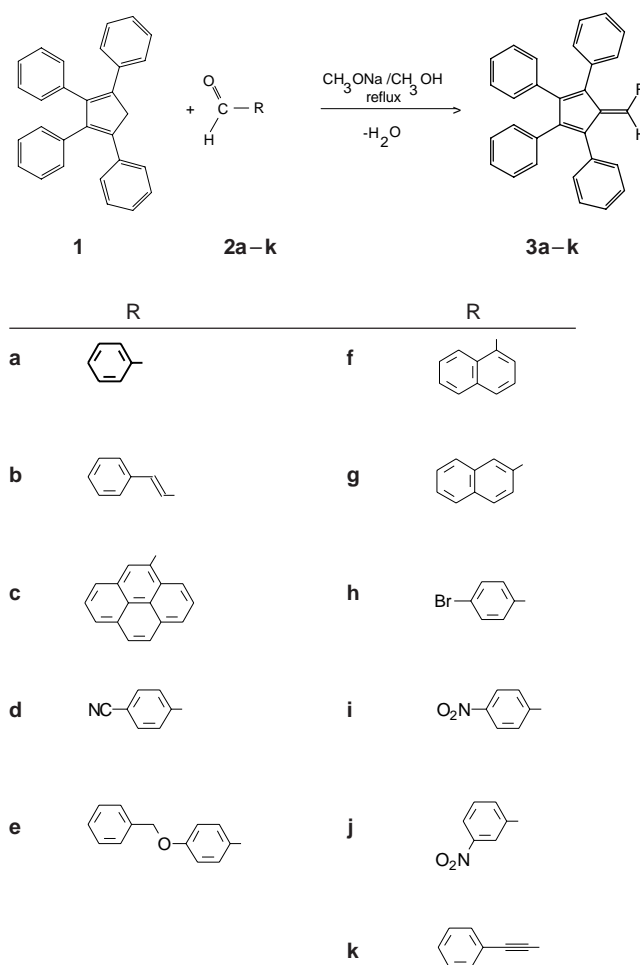
The fulvenes **3** are of orange to deep red colour. Some of them can be sublimated, which results in somewhat higher glass temperatures (T_g) after sublimation (**3a**: 98 °C, **3c**: 138 °C). A probable reason for this observation might be the higher rate of cooling during sublimation than in the DSC experiment, which may have an influence on the structure of the glasses. In the second heating run in the DSC apparatus the sublimated samples have the same glass temperatures as before sublimation. Therefore, the different glass temperatures before and after sublimation are not caused by additional purification of the sample during sublimation.

Experimental

Synthesis of Fulvenes (General Procedure)

In a three necked round bottomed flask equipped with a reflux condenser and a dropping funnel, calculated amounts of 1,2,3,4-tetra-phenylcyclopenta-1,3-diene and the respective aldehyde were dissolved in abs. methanol and heated to reflux, followed by addition of sodium methoxide as a 4 wt.% solu-

tion in methanol during a period of 30 min. After refluxing for a given period of time, the mixture was cooled to room temperature. The precipitated crystals were filtered by suc-



Scheme 1 Synthesis of fulvenes **3** from 1,2,3,4-tetra-phenylcyclopenta-1,3-diene (**1**) and aldehydes **2**

Table 1 Glass-forming Fulvenes (**3a–k**)

Compound	Formula	Molar mass (g mol ⁻¹)	Reaction time (h)	Yield (%)	T _m (°C)	T _g (°C)
3a	C ₃₆ H ₂₆	458.6	6	95	202	81
3b	C ₃₈ H ₂₆	484.6	5.5	74	197	91
3c	C ₄₆ H ₃₀ O	582.7	10	46	279	120
3d	C ₃₇ H ₂₅ N	483.6	7	94	225	88
3e	C ₄₃ H ₃₂ O	564.7	18	26	164	74
3f	C ₄₀ H ₂₈	508.7	6	88	217	94
3g	C ₄₀ H ₂₈	508.7	6	90	198	91
3h	C ₃₆ H ₂₅ Br	537.5	6	94	185	84
3i	C ₃₆ H ₂₅ NO ₂	503.6	6	79	220	95
3j	C ₃₆ H ₂₅ NO ₂	503.6	6	84	159	82
3k	C ₃₈ H ₂₆	482.6	3	87	177 (dec.)	97 ^{a)}

^{a)} Determined after sublimation.

tion and washed three times with methanol before drying *in vacuo* at 40 °C for 24 h. Yields, melting points, and glass transition temperatures are compiled in Tab. 1.

1,2,3,4,6-Pentaphenylfulvene (**3a**)

The reaction was carried out with 1.85 g (5 mmol) 1,2,3,4-tetraphenylcyclopenta-1,3-diene, 3.70 g (39 mmol) benzaldehyde in 25 ml abs. methanol, and 90 ml (ca. 56 mmol) sodium methoxide as 4 wt.% solution in methanol (reflux time 6 h); yield 2.18g (95%), *m.p.* 202 °C (lit. [9]: 203–204 °C), T_g 81 °C. – ¹H NMR: δ/ppm = 6.78–7.42 (m, 26H, Ar–H and –C–H). – MS: *m/e* = 458 (M⁺).

C₃₆H₂₆ Calcd.: C 94.29 H 5.71
(458.6) Found: C 94.44 H 5.71.

1,2,3,4-Tetraphenyl-6-(2-phenylvinyl)fulvene (**3b**)

The reaction was carried out with 1.85 g (5 mmol) 1,2,3,4-tetraphenylcyclopenta-1,3-diene, 5.29 g (40 mmol) cinnamaldehyde in 45 ml abs. methanol, and 90 ml (ca. 56 mmol) sodium methoxide as 4 wt.% solution in methanol (reflux time 5.5 h); yield 1.80g (74%), *m.p.* 197 °C (lit. [10]: 193–194 °C), T_g 91 °C. – ¹H NMR: δ/ppm = 6.63–6.65 (d, 1H, –C–H), 6.76–6.78 (d, 1H, –C–H), 6.80–7.40 (m, 26H, Ar–H and –C–H). – MS: *m/e* = 484 (M⁺).

C₃₈H₂₆ Calcd.: C 94.18 H 5.82
(484.6) Found: C 94.41 H 5.84.

1,2,3,4-Tetraphenyl-6-(pyren-1-yl)fulvene (**3c**)

The reaction was carried out with 1.85 g (5 mmol) 1,2,3,4-tetraphenylcyclopenta-1,3-diene, 2.30 g (10 mmol) pyrene-1-carbaldehyde in 60 ml abs. methanol, and 90 ml (ca. 56 mmol) sodium methoxide as 4 wt.% solution in methanol (reflux time 10 h); yield 1.33 g (46%), *m.p.* 279 °C, T_g 120 °C. – ¹H NMR: δ/ppm = 6.35–8.22 (m, 30H, Ar–H and –C–H). – MS: *m/e* = 582 (M⁺).

C₄₆H₃₀O Calcd.: C 94.81 H 5.19
(582.7) Found: C 94.97 H 5.16.

6-(4-Cyanophenyl)-1,2,3,4-tetraphenylfulvene (**3d**)

The reaction was carried out with 0.93g (2.5 mmol) 1,2,3,4-tetraphenylcyclopenta-1,3-diene, 1.31 g (10 mmol) 4-cyanobenzaldehyde in 30 ml abs. methanol, and 45 ml (ca. 28 mmol) sodium methoxide as 4 wt.% solution in methanol (reflux time 7 h); yield 1.14g (94%), *m.p.* 225 °C, T_g 88 °C. – ¹H NMR: δ/ppm = 6.77–7.37 (m, 25H, Ar–H and –C–H). – MS: *m/e* = 483 (M⁺).

C₃₇H₂₅N Calcd.: C 91.89 H 5.21 N 2.90
(483.6) Found: C 92.06 H 5.15 N 2.96.

6-(4-Benzyloxyphenyl)-1,2,3,4-tetraphenylfulvene (**3e**)

The reaction was carried out with 1.85 g (5 mmol) 1,2,3,4-tetraphenylcyclopenta-1,3-diene, 3.18 g (15 mmol) 4-benzyloxybenzaldehyde in 30 ml abs. methanol, and 45 ml (ca. 28 mmol) sodium methoxide as 4 wt.% solution in methanol (reflux time 18 h); yield 0.73g (26%), *m.p.* 164 °C, T_g 74 °C. – ¹H NMR: δ/ppm = 4.96 (s, 2H, –CH₂–), 6.48–7.61 (m, 30H, Ar–H and –C–H). – MS: *m/e* = 564 (M⁺).

C₄₃H₃₂O Calcd.: C 91.46 H 5.71
(564.7) Found: C 91.21 H 5.58.

6-(1-Naphthyl)-1,2,3,4-tetraphenylfulvene (**3f**)

The reaction was carried out with 0.93g (2.5 mmol) 1,2,3,4-tetraphenylcyclopenta-1,3-diene, 1.56 g (10 mmol) naphthalene-1-carbaldehyde in 30 ml abs. methanol, and 45 ml (ca. 28 mmol) sodium methoxide as 4 wt.% solution in methanol (reflux time 6 h); yield 1.12g (88%), *m.p.* 217 °C (lit. [10]: 209–211 °C), T_g 94 °C. – ¹H NMR: δ/ppm = 6.56–8.17 (m, 28H, Ar–H and –C–H). – MS: *m/e* = 508 (M⁺).

C₄₀H₂₈ Calcd.: C 94.45 H 5.55
(508.7) Found: C 94.41 H 5.46.

6-(2-Naphthyl)-1,2,3,4-tetraphenylfulvene (**3g**)

The reaction was carried out with 0.93 g (2.5 mmol) 1,2,3,4-tetraphenylcyclopenta-1,3-diene, 1.56 g (10 mmol) naphthalene-2-carbaldehyde in 30 ml abs. methanol, and 45 ml (ca. 28 mmol) sodium methoxide as 4 wt.% solution in methanol (reflux time 6 h); yield 1.14 g (90%), *m.p.* 198 °C, T_g 91 °C. – ¹H NMR: δ/ppm = 6.55–7.64 (m, 28H, Ar–H and –C–H). – MS: *m/e* = 508 (M⁺).

C₄₀H₂₈ Calcd.: C 94.45 H 5.55
(508.7) Found: C 94.34 H 5.39.

6-(4-Bromophenyl)-1,2,3,4-tetraphenylfulvene (**3h**)

The reaction was carried out with 0.93 g (2.5 mmol) 1,2,3,4-tetraphenylcyclopenta-1,3-diene, 1.85 g (10 mmol) 4-bromobenzaldehyde in 30 ml abs. methanol, and 45 ml (ca. 28 mmol) sodium methoxide as 4 wt.% solution in methanol (reflux time 6 h); yield 1.26 g (94%), *m.p.* 185 °C, T_g 84 °C. – ¹H NMR: δ/ppm = 6.76–7.33 (m, 25H, Ar–H and –C–H). – MS: *m/e* = 536/538 (M⁺).

C₃₆H₂₅Br Calcd.: C 80.45 H 4.69
(537.5) Found: C 80.05 H 4.51.

6-(4-Nitrophenyl)-1,2,3,4-tetraphenylfulvene (3i)

The reaction was carried out with 0.93 g (2.5 mmol) 1,2,3,4-tetraphenylcyclopenta-1,3-diene, 1.51 g (10 mmol) 4-nitrobenzaldehyde in 30 ml abs. methanol, and 45 ml (ca. 28 mmol) sodium methoxide as 4 wt.% solution in methanol (reflux time 6 h); yield 1.00 g (79%), *m.p.* 220 °C (lit. [10]: 227–228 °C), *T_g* 95 °C. – ¹H NMR: δ/ppm = 6.78–7.74 (m, 25H, Ar- and -C-H). – MS: *m/e* = 503 (M⁺), 487 (M⁺ – O).
C₃₆H₂₅NO₂ Calcd.: C 85.86 H 5.00 N 2.78
(503.6) Found: C 87.47 H 4.94 N 2.50.

6-(3-Nitrophenyl)-1,2,3,4-tetraphenylfulvene (3j)

The reaction was carried out with 0.93 g (2.5 mmol) 1,2,3,4-tetraphenylcyclopenta-1,3-diene, 1.51 g (10 mmol) 3-nitrobenzaldehyde in 30 ml abs. methanol, and 45 ml (ca. 28 mmol) sodium methoxide as 4 wt.% solution in methanol (reflux time 6 h); yield 1.09 g (84%), *m.p.* 159 °C, *T_g* 82 °C. – ¹H NMR: δ/ppm = 6.78–7.83 (m, 25H, Ar-H and -C-H). – MS: *m/e* = 503 (M⁺).
C₃₆H₂₅NO₂ Calcd.: C 85.86 H 5.00 N 2.78
(503.6) Found: C 85.79 H 4.95 N 2.77.

1,2,3,4-Tetraphenyl-6-(phenylethynyl)-fulvene (3k)

The reaction was carried out with 1.85 g (5 mmol) 1,2,3,4-tetraphenylcyclopenta-1,3-diene, 1.95 g (15 mmol) phenylpropargylaldehyde in 50 ml abs. methanol, and 90 ml (ca. 56 mmol) sodium methoxide as 4 wt.% solution in methanol (reflux time 3 h); yield 2.09 g (87%), *m.p.* 177 °C (dec.), *T_g* 97 °C (after sublimation). – MS: *m/e* = 482 (M⁺).
C₃₈H₂₆ Calcd.: C 94.57 H 5.43
(482.6) Found: C 93.64 H 5.45.

Analyses

¹H NMR spectra were obtained on a Bruker WM-300 instrument at 300 MHz with CDCl₃ as solvent and tetramethylsilane as internal standard. Mass spectra were obtained on a Varian 311A instrument in the field-desorption modus. Elemental analyses were performed on a Perkin Elmer 240 ele-

ment analyser. Melting points and glass transitions were determined by differential scanning calorimetry (DSC) using a Du Pont 912 thermal analyser. Samples of 5–10 mg in polycrystalline form as received from synthesis were put into aluminium pans and heated with a rate of 10 K min⁻¹ under a nitrogen flow. In the first heating run the melting points and their enthalpy changes were measured. Indium metal was used as a standard. After melting, the samples were cooled with a cooling rate of approximately 20 K min⁻¹. The resulting glasses were heated under the same conditions again to measure the glass transition temperatures.

References

- [1] K. Naito, A. Miura, *J. Phys. Chem.* **1993**, *97*, 6240
- [2] K. Naito, *Chem. Mater.* **1994**, *6*, 2343
- [3] Part II: I. Alig, D. Braun, R. Langendorf, H. O. Wirth, M. Voigt, J. H. Wendorff, *J. Mater. Chem.* **1998**, *8*, 847
- [4] D. Braun, R. Langendorf, *J. Prakt. Chem.* **1999**, *341*, 128
- [5] H. Inada, Y. Shirota, *J. Mater. Chem.* **1993**, *3*, 319
- [6] K. Nishimura, T. Kobata, H. Inada, Y. Shirota, *J. Mater. Chem.* **1991**, *1*, 897
- [7] D. W. Van Krevelen, "Properties of Polymers", 3rd Edn., Elsevier, Amsterdam, New York 1990, Chapter 6, p. 129
- [8] F. Bueche, "Physical Properties of Polymers", 1st Edn., Interscience Publishers, New York 1962, p. 85
- [9] W. Dilthey, P. Huchtemann, *J. Prakt. Chem.* **1940**, *154*, 238
- [10] D. Taber, N. Picus, E. I. Becker, P. E. Spoerri, *J. Am. Chem. Soc.* **1955**, *77*, 1010

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